CONTRACT REPORT NUMBER 69055-01-ST

CONTRACTOR: McGill University

REQUISITION NUMBER 23440-6-9055

DEVELOPMENT OF REDUCTIVE PRECIPITATION PROCESS FOR PRODUCTION OF HIGH PURITY GOLD, PLATINUM AND PALLADIUM POWDERS

by

G.P. Demopoulos

Department of Mining and Metallurgical Engineering
McGill University
Montreal, Quebec

Work on the project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

DSS Contract Serial No. 23440-6-9055/01-ST.

March 1988.

72 pp

MICROMEDIA

Contents

		Page
	Executive Summary	i
1.	INTRODUCTION	1
2.	THEORETICAL CONSIDERATIONS	4
3.	EXPERIMENTAL	8
4.	RESULTS AND DISCUSSION	14
	PART A: SINGLE METAL SOLUTIONS	14
	GOLD	14
	PALLADIUM	17
	PLATINUM	21
	PART B: BINARY METAL SOLUTIONS	37
	PART C: DEPOSITION OF THIN METAL FILMS ON CERAMIC SUBSTRATES	57
5.	CONCLUSIONS AND RECOMMENDATIONS	62

Executive Summary

The recovery of gold, platinum, and palladium as powders by hydrogen precipitation has been studied in relation to a solvent extraction process recently developed by CANMET for the separation of precious metals from chloride contaminated liquors.

More specifically in the present work the strengths and limitations of hydrogen reduction in recovering those metals in a powder form from solvent extraction purified or contaminated (without prior treatment with solvent-extraction) liquors have been established. The most important findings of the present work are :

(i) Hydrogen reduction is a very effective and attractive method for the precipitation of platinum and palladium from the respective single metal purified strip liquors. The precipitation kinetics are very fast and only mild temperature (25 - 50^{o}C) and H_2 pressure (15 - 50 psi) conditions are required. So no expensive autoclaves but rather commercially available glass or ceramic coated reactors are well suited for this type of operation. Moreover the metals are recovered in fine powder form which seem to possess good properties for application in the electronic thick film conductor industry. An additional advantage of recovering Pt and Pd from the strip liquors by hydrogen reduction is the fact that no neutralization or prior solution adjustment is required. Other chemical precipitating agents in general require neutralization which is rather

prohibitive considering in particular the high acid concentration (6 - 8N HCl) of the Pd strip solutions.

(ii) Gold precipitation by hydrogen reduction was again found to be virtually complete under relatively mild conditions but unfortunately the product is not in powder form which thus imposes problems into recovering it.

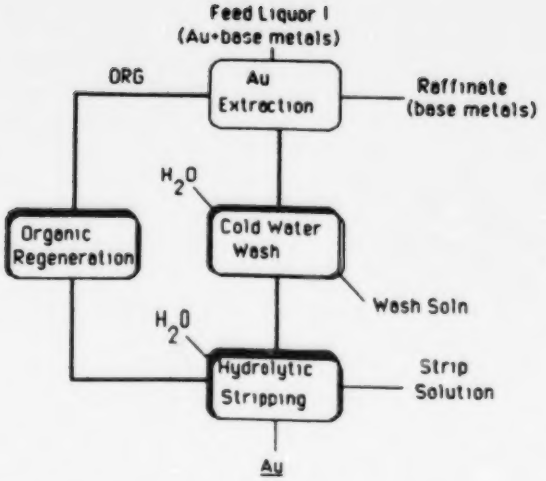
(iii) Selective precipitation of Pt and Pd in the presence of several common impurity elements such as Fe, Cu, Pb, Sb, As and Bi is not possible by hydrogen reduction. Neither can the separation of Pt and Pd be accomplished by the same. Thus hydrogen reduction is attractive as a recovery method only after solvent extraction has been used to purify and separate the precious metals.

(iv) Finally some preliminary results indicate that hydrogen reduction of Pt or Pd chloride solutions can be successfully used to prepare composite materials (thin metal coatings on ceramic substrates) provided that reduction is carried out in a liquid layer rather than in the bulk of the solution. Further work is warranted.

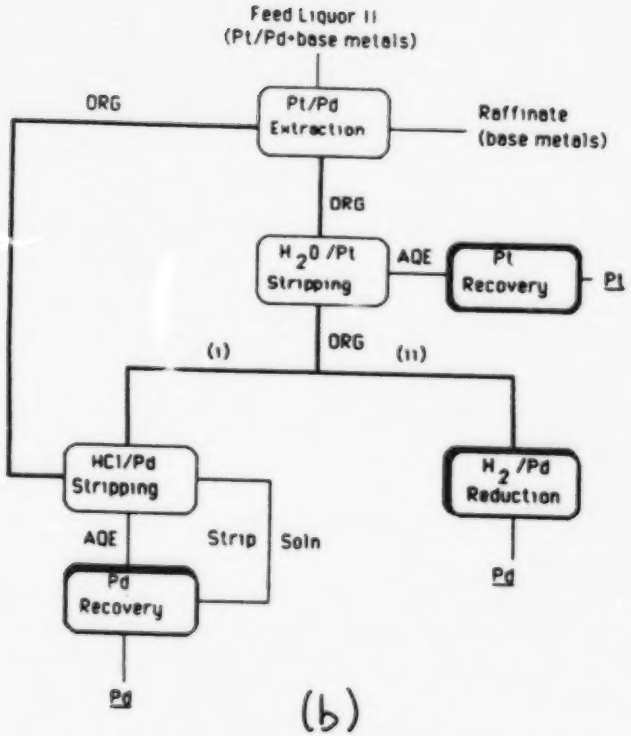
1. INTRODUCTION

Due to their outstanding physicochemical properties, such as catalytic activity, conductivity and corrosion/oxidation resistance precious metals find today extensive usage outside of the traditional jewellery and investment industries. The increasing use of precious metals in such areas as electronics and catalysis, as well as their high value, has led to an increased interest in their separation and recovery. Fine precious metal powders are in particular used in the electronics industry for the manufacturing of fired conductors by thick film technology. Most of these precious metal powders are prepared by reductive precipitation from their respective aqueous chloride solutions (2). On the other hand separation and recovery of the precious metals has been achieved traditionally by chemical salt precipitation or more recently with the aid of solvent extraction reagents (3).

Very recently a new solvent extraction process was developed for the refining of gold and platinum group metals which makes use of commercially available alkylated derivatives of 8-hydroxyquinoline (8-HQ; Lix 26 or Kelex 100) (4),(5),(6). By employing this solvent extraction system purified organic and aqueous solutions of Au(III), Pt(IV) and Pd(II) are produced from which the metals have to be recovered. In Fig. 1 the flowsheets considered for the purification of gold (a) and platinum/palladium (b) by this SX route are shown. Alternative methods could be used for the recovery of the metals from their



(a)



(b)

Fig. 1 Purification schemes for gold (a) and platinum/palladium (b) incorporating solvent extraction and precipitation.

purified solutions. These are: (i) direct recovery of Au from the loaded organic phase by hydrolytic stripping (box "Hydrolytic stripping" in Fig. 1(a)). (ii) direct recovery of Pd from the loaded organic phase by hydrogen reduction (box "H_2/Pd Reduction" Fig. 1(b)) and (iii) precipitation of Pt and Pd from the aqueous strip chloride liquors by hydrogen reduction (boxes "Pt Recovery" and "Pd Recovery" in Fig. 1(b)).

Methods (i) and (ii) have been already examined and the experimental results have been reported (7,8). These methods produce gold and palladium powders with very good morphological characteristics having the potential of funding applications in the electronics industry (9). However, they suffer from alteration of the extractant molecule (oxidation in the case of Au and reduction in the case of Pd) thus necessitating regeneration. This remains yet to be investigated.

Method (iii) constitutes the subject of the present contract report. The specific objectives of the present work were

(i) to determine the technical feasibility of producing Au, Pt, and Pd powders by H_2 reduction of their chloride salt solutions and

(ii) to evaluate the feasibility of selectively precipitating the precious metals vis-a-vis various contaminant base elements that are commonly encountered in the refining industry.

2. THEORETICAL CONSIDERATIONS

Previous Work

Hydrogen is well known for its ability to reduce precious metals from their aqueous salt solutions. The Ipatiefs first (1909-31) and later Tronev and his coworkers (1930-1951) are well known for their pioneering work in hydrogen reduction of noble and other metals (10). Ipatieff, Jr. and Tronev (11) reported first on the precipitation of Pd(II), Pt(IV), Ir(III), Ir(IV) and Rh(III) from chloride solutions. The relative ease of precipitation was found to increase in the followilng order Ir < Pt < Rh < Pd. Later the same authors reported on the separation of the platinum metals with hydrogen (12). They considered the following binary metal chloride solutions: (i) Pd(II)/Cu(II), (ii) Pd(II)/Fe(III), (iii) Pd(II)/Pt(IV), (iv) Pd(II)/Ir(IV), (v) Pd(II)/Ir(III), (vi) Rh(III)/Ir(IV), and (vii) Pd(II)/Rh(III). They found Pd to precipitate selectively in most of the cases [(i) to (v)], Rh to precipitate selectively from Ir(IV) [(vi)] but separation was not possible in case (vii). Finally Tronev and Bondin (13) reported on the reduction of gold from chloride solutions with hydrogen under pressure as well. Very recently Findlay (14) reported more information on the recovery of precious metals by hydrogen reduction from their respective single chloride salt solutions. He found metals to precipitate in the following order Pd(II) > Rh(III) > Ru(III) Pt(IV) from their solutions of IN HCl by raising the

temperature respectively to 20°, 30° and 80°C and using 1 atm H_2. Finally in a recent japanese patent the use of H_2 to recover Pd and Pt from a chloride leach solution originating from the treatment of spent catalysts was proposed (15). Others it is believed have also used hydrogen to recovery precious metals but no actual procedures have been described. A critical aspect of metal precipitation from solution is avoiding plating and plastering of the metal on the walls of the reactor vessel. However, no information as to the physical characteristics of the metal precipitates nor the nucleation and growth phenomena involved in their formation have been described previously.

Thermodynamics

Thermodynamically the reduction of noble metals with hydrogen is highly favourable as it is demonstrated with the standard potentials listed in Table 1.

Table 1. Standard reduction potentials of precious metal chlorides (16)

Metal Couple	E°(V)
$AuCl_4^-/Au$	1.002
$IrCl_6^{2-}/Ir$	0.86
$IrCl_6^{3-}/Ir$	0.86
$PtCl_6^{2-}/Pt$	0.75
$PtCl_4^{2-}/Pt$	0.76
$PdCl_4^{2-}/Pd$	0.62
$RhCl_6^{3-}/Rh$	0.5

The actual reduction potential depends of course on the acid (H^+) and salt (Cl^-) concentrations prevailing in the PM solution:

$$MCl_x^{(x-z)-} + \frac{z}{2} H_2 \rightarrow M + xCl^- + zH^+ \qquad (1)$$

$$E_{(1)} = E^{o}_{MClx^{(x-z)-}/M^{o}} - \frac{RT}{zF} \ln \frac{\alpha_{Cl^-}^{x} \; \alpha_{H^+}^{z}}{\alpha_{MCl_x^{(x-z)-}} \; P_{H_2}^{z/2}} \qquad (2)$$

The higher the quantities α_{Cl^-} and α_{H^+} the lower $E_{(1)}$ would be and consequently the lower the driving reduction force would be. On the other hand the higher the metal concentration, i.e. $\alpha_{MCl_x^{(x-z)-}}$ and the higher the hydrogen pressure the higher the driving reduction force.

Thus using the F*A*C*T Facility at McGill we were able to calculate the following changes in the reduction potential Pt(II)/Pt(0) as a function of α_{Cl^-} in the pH region 0-6.

Table 2. The reduction potential of $PtCl_4^{2-}/Pt^o$ as a function of a_{Cl^-} (25°C)

$PtCl_4^{2-}/Pt(0)$ E(V)	a_{Cl^-}	$a_{PtCl_4^{2-}}$
0.9	10^{-3}	10^{-2}
0.9	10^{-2}	10^{-2}
0.8	10^{-1}	10^{-2}
0.72	10^{0}	10^{-2}
0.69	3×10^{0}	10^{-2}
0.65	6×10^{0}	10^{-2}
0.75	10^{0}	10^{-1}
0.71	10^{0}	10^{-3}
0.68	10^{0}	$10^{-<1}$

Catalysis

Although the mechanism of precipitation of precious metals by hydrogen reduction has not been studied previously, nevertheless a number of studies have been conducted on the ability of dissolved precious metals to activate hydrogen - the latter is of critical importance since it would determine if homogeneous or heterogeneous nucleation would take place. Thus Halpern and his co-workers in a series of investigations found molecular hydrogen to be activated by $PdCl_4^{2-}$ (17), $RhCl_6^{3-}$ (18) and

$RuCl_6^{3-}$ (19). However $PtCl_6^{2-}$ (20), $IrCl_6^{3-}$, $IrCl_6^{2-}$ and $AuCl_4^-$ (21) were found to be inactive. In terms of heterogeneous catalytic activity though all the precious metals are good hydrogenation catalysts with the exception of gold (21,22). From Halpern's (17,18) and Findlay's results (14) it appears the homogeneous catalytic activity to increase in the order of Pt(IV) < Rh(III) < Pd(II).

3. EXPERIMENTAL

The aqueous precious metal chloride solutions were prepared by dissolving gold, palladium, or platinum metal in aqua regia, evaporating the nitrates and solubilizing the metal salts in HCl-NaCl media. Single as well as binary metal solutions were used. The single-metal hydrogen reduction tests were conducted in a 450 ml stainless steel autoclave equipped with glass liner and internal metal parts made of titanium.

Previous investigators (11,12,13,14) have used poorly agitated autoclaves without provision for continuous supply of H_2 at constant pressure. Good agitation (effective transfer of H_2 from the gas phase to the solution) and maintenance of constant H_2 pressure are an important precondition for any

reliable kinetic study. Their results, therefore, will have to be considered only partially valid. It was due to these reasons that special attention was devoted in the present work to make certain that gas dissolution was not a limiting factor. To this end first the dissolution kinetics of H_2 in HCl-NaCl media was started. Figure 2 shows data for hydrogen dissolving in HCl-NaCl solutions at 25°C using 450 rpm stirring rate. Dissolved hydrogen concentrations were calculated by application of the ideal gas law, knowing the pressure drop in the sealed autoclave and its gas volume. In general, hydrogen dissolved very fast only when a high overpressure was applied (Fig. 2). At 50 psi at which pressure most of the experiments were carried out the dissolution rate was intermediate. H_2 solubility as it was expected was proportional to hydrogen partial pressure (Henry's law). More data on the solubility of H_2 in aqueous chloride solutions can be found in reference 23. To avoid therefore interference of the slow hydrogen dissolution rate with the measurement of the chemical precipitation rate (reduction rate) the following procedure was adopted. A blank NaCl solution was saturated with H_2 for 1 hour and then a predetermined small value of concentrated PM/HCl solution was added using a specially adapted pressure chamber and the experiment was started ($t = 0$).

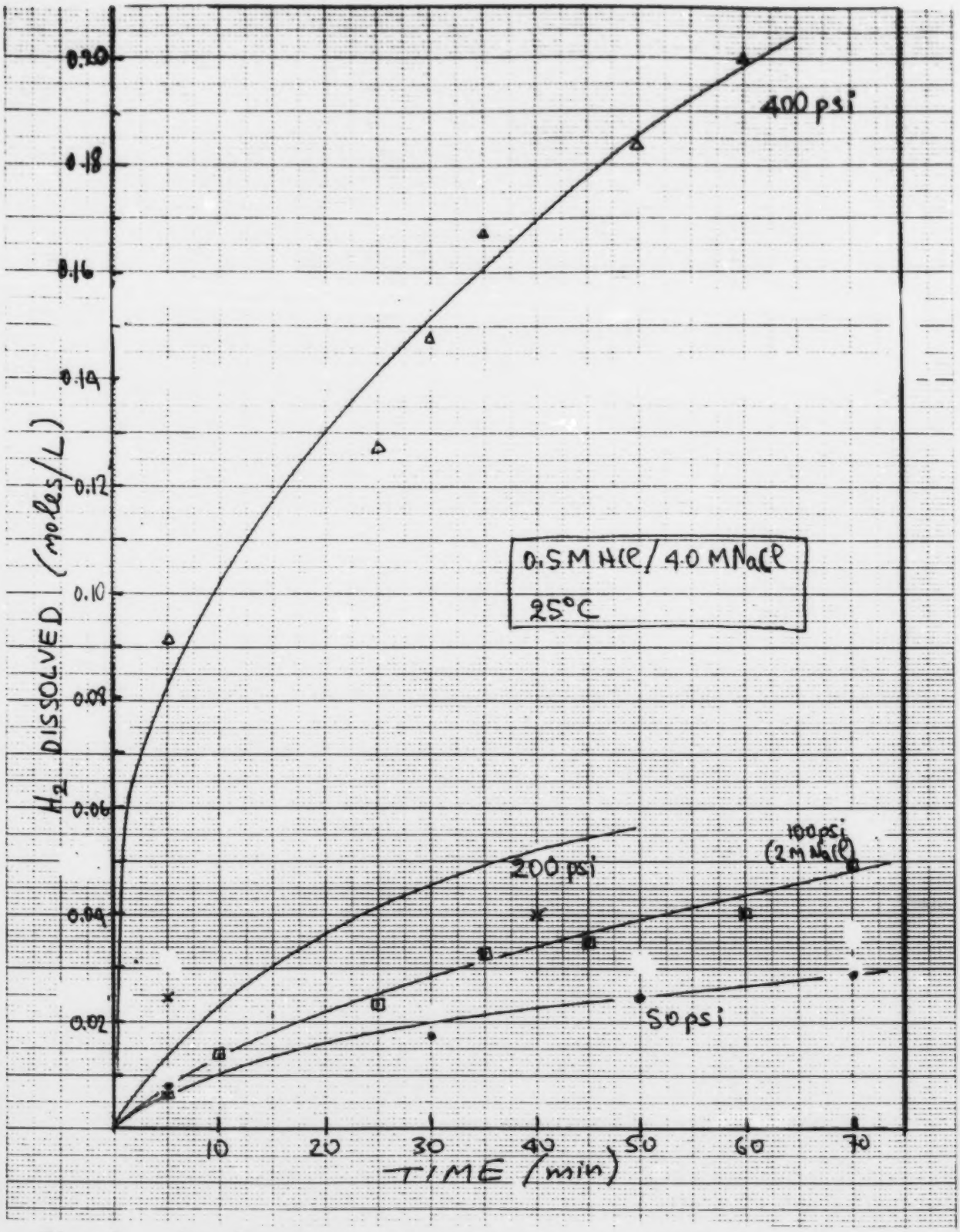


Fig. 2 The dissolution of hydrogen gas in HCl/NaCl media at various pressures.

The precipitation kinetics were followed by taking periodically solution samples and analysing them for metal content by AA spectrophotometry. Analysis of all the metals investigated in this work was straightforward apart from that of Pt. The problem of Pt analysis by AA was in particular difficult in the presence of NaCl. Strong interferences were observed resulting in non-linear calibration curves and suppressed absorbance values. The problem is exemplified with the calibration curves shown in Fig. 3 ((a) no NaCl, (b) with NaCl). The problem was satisfactorily circumvented by adapting the use of 1-2 g/l La^{3+} in all Na-containing samples and preparing standards with exactly the same matrix with the samples to be analysed. Some typical calibration curves obtained with the use of La^{3+} are shown in Fig. 4. Finally the calculated Pt concentration values had to be corrected proportionally on the basis of first sample (t = 0) for which the concentration (in most of the experiments equal to 1 g/l) was already known. A thorough discussion of the interferences experienced in the determination of Pt by AA is given in ref. 24.

The metal powders produced were washed with distilled water and dried prior to being subjected to SEM examination. In conjunction with the latter gold coating of the specimens was practiced in order to get better overall characterization of the metal particles.

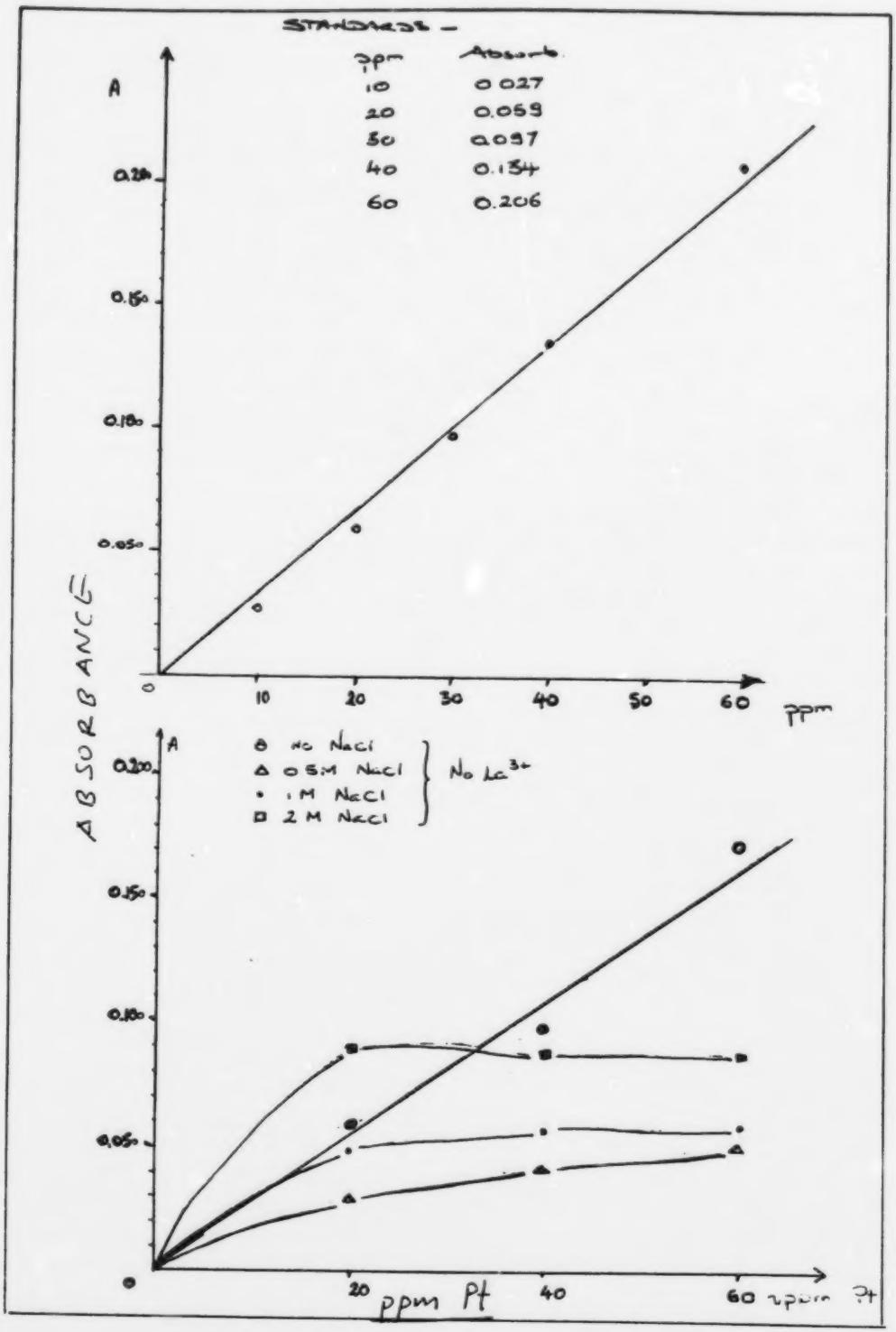


Fig. 3 Typical AA calibration curves obtained for Pt with no NaCl (a) and with NaCl (b). No La^{3+} added.

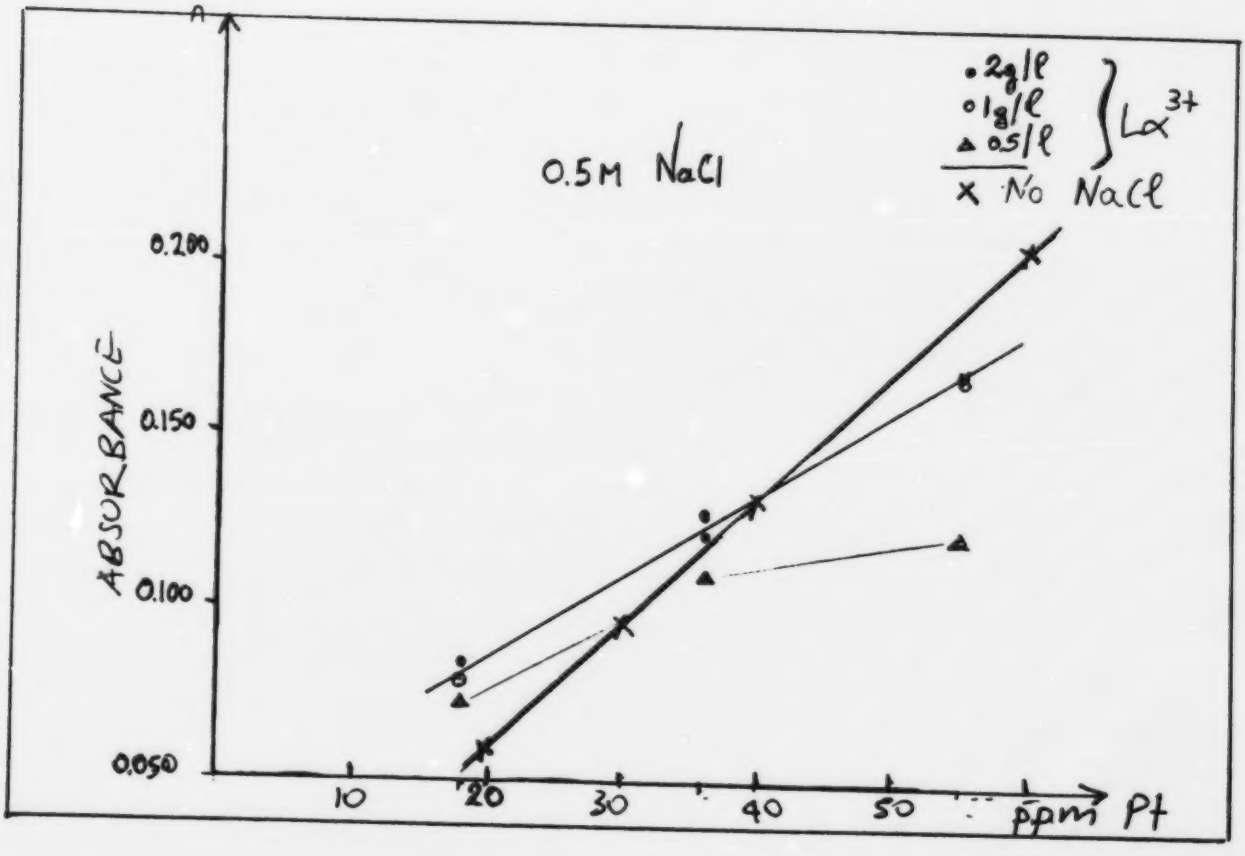


Fig. 4 Pt calibration curves in the presence of NaCl (0.5 M) and 1 - 2 g/l La^{3+} additions.

4. RESULTS AND DISCUSSION

PART A: SINGLE METAL SOLUTIONS

In this part the precipitation of Au, Pd and Pt by hydrogen reduction of their respective single metal solutions is described.

GOLD

Au(III) solutions (1 g/l) of varying HCl (0.5 - 1.5 M) and NaCl (0 - 2M) concentrations were reduced at temperatures 25 and 60^{o}C with hydrogen under 350 kPa (50 psi) pressure. The results obtained are illustrated in Fig. 5. Metal precipitation took place to almost completion under most of the reduction conditions tested but not metal powder was observed to form. Instead most of the metal was found to be plated on the internal metal parts of the autoclave (Ti) and the rest of it was recovered as a massive non-particulate precipitate (Fig. 6). Attempts to produce gold powder by adding in the solution a surface active substance (anthraquinone) were unsuccessful.

The failure of H_2 to precipitate particulate gold from chloride solution is attributed to the inability of $AuCl_4^-$ to

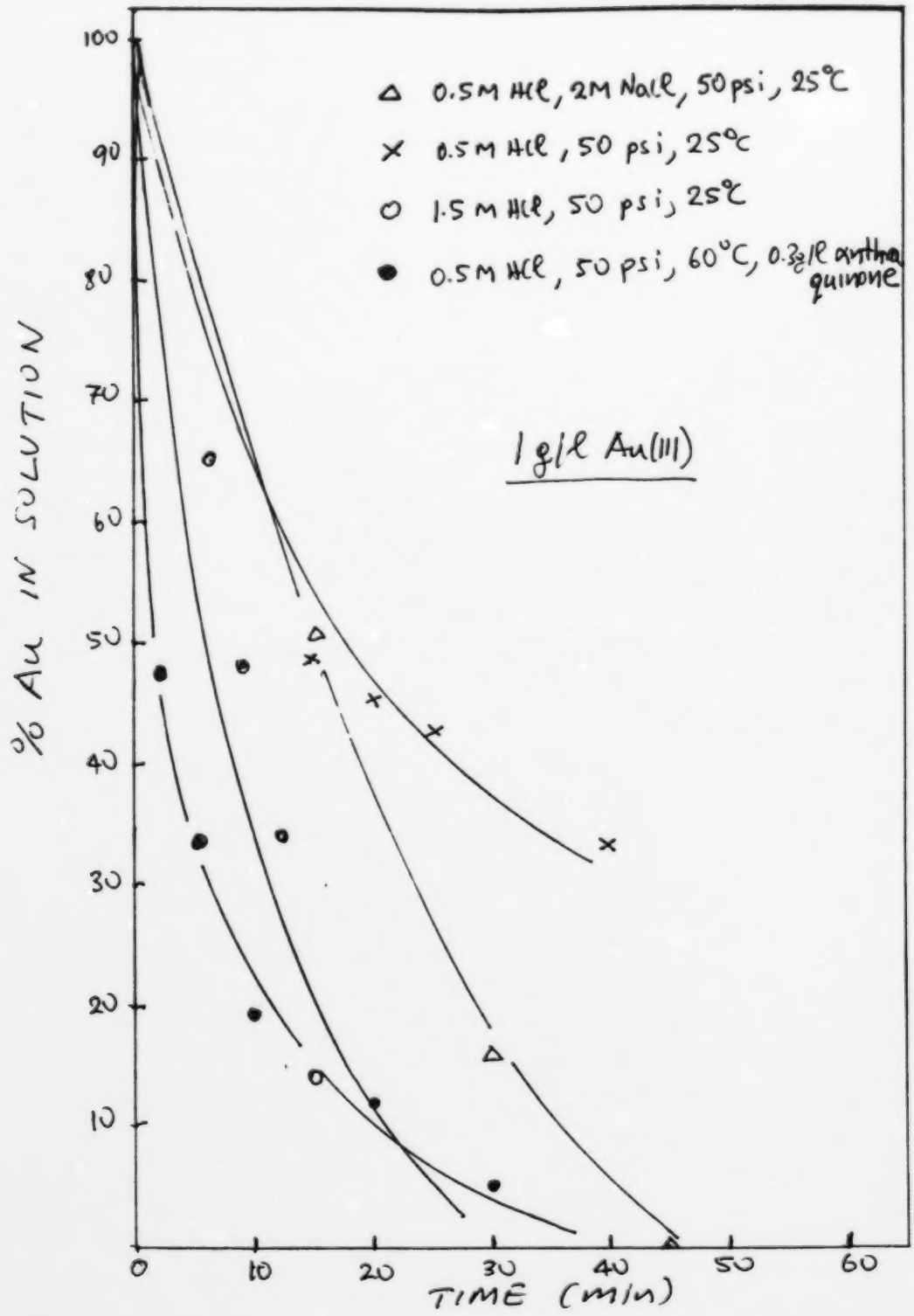


Fig. 5 Precipitation of Au from chloride liquors by hydrogen reduction (1 g/l Au(III)).

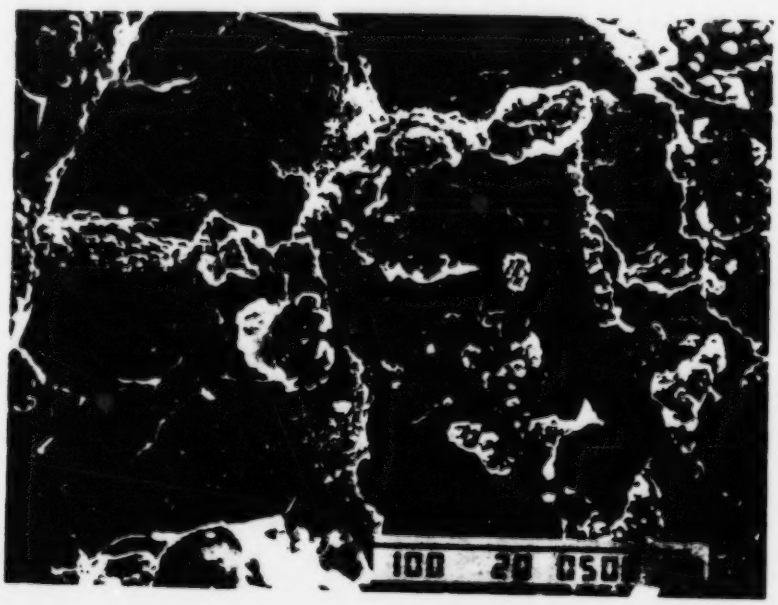


Fig. 6 Massive gold precipitate produced by hydrogen reduction.

act as a homogeneous catalyst for the activation of molecular hydrogen (see "Theoretical Considerations" section). Homogeneous activation of H_2 via the formation of an intermediate hydride complex (precursor complex) is considered vital in producing discrete metal particles. It is of interest to note here that when SO_2 is used as a reducing agent, production of gold powder is possible (25, 26). This might be the result of the ability of SO_2 to form the following intermediate complex $Au(SO_3)^{5-}$ (27).

PALLADIUM

Precipitation of Pd from HCl-NaCl media was found to be extremely fast taking less than 5 minutes for complete metal recovery even at high acid and salt concentrations (up to 6M HCl and 3M NaCl) with only 350 kPa H_2 and room temperature operation. Typical results are plotted in Fig. 7. Quantitative recovery of the metal as powder was possible with no plating observed to occur. SEM examination revealed the powder to consist mostly of spherical particles of varying size (0.2 to 2.0 μm) exhibiting smooth or spiked morphology. In general, low ionic strength solutions (no NaCl present) found to give spiked particle morphology of approximately 1.5 μm average diameter (Fig. 8a). In the presence of NaCl the average diameter

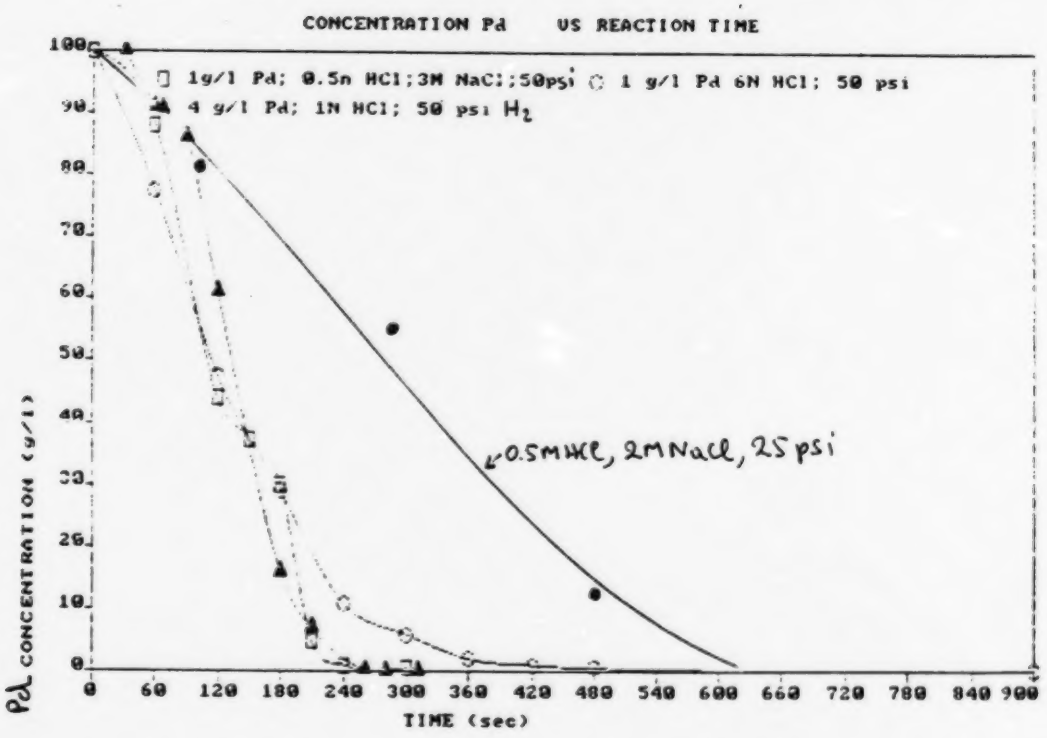


Fig. 7 Precipitation of Pd from chloride liquors by hydrogen reduction (25°C).

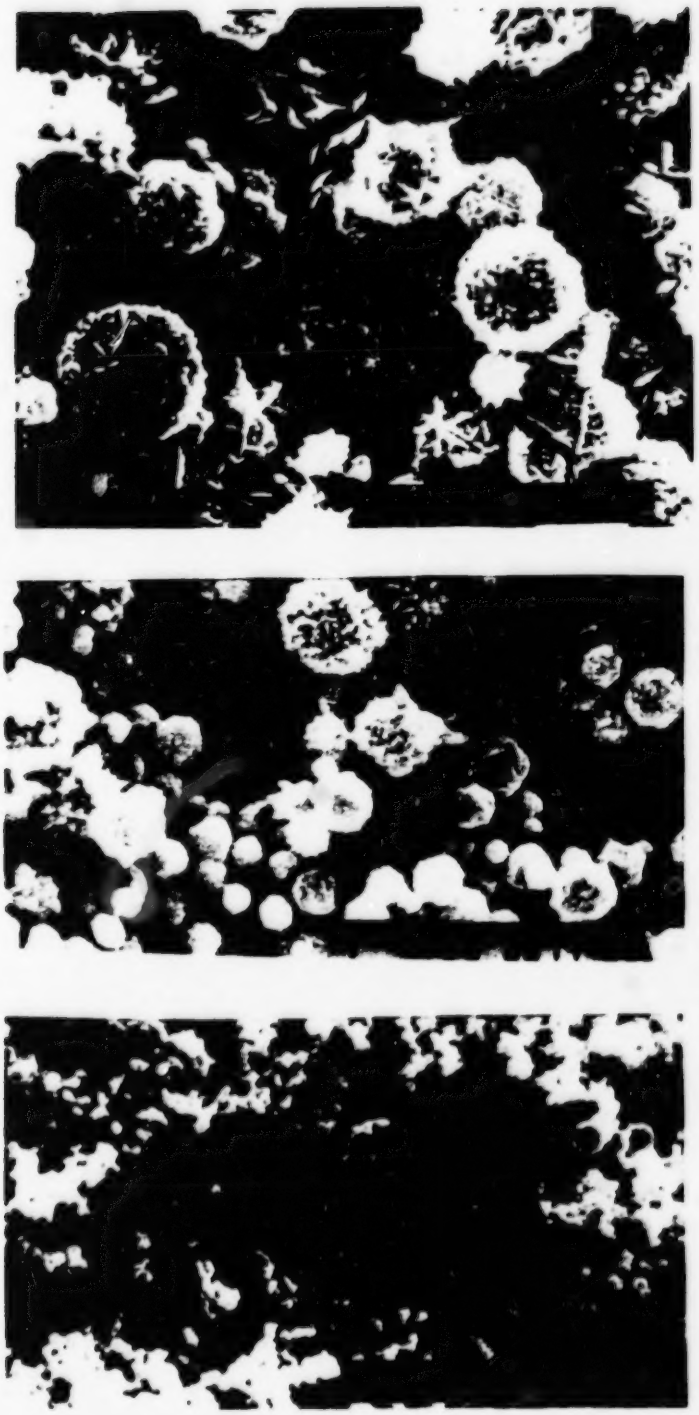


Fig. 8 Palladium powders precipitated from chloride liquors by hydrogen reduction (a) 1 M HCl, 25°C, (b) 0.5 M HCl 2.0 M NaCl, 25°C, (c) 0.5 M HCl, 1.0 M NaCl, 25°C, 0.5 g/l Anthraquinone.

of the particles shifted to lower size ($\sim$ 0.8 μm) and the spiked morphology was considerably reduced (Fig. 8b). Completely smooth particles were obtained when an organic additive (anthaquinone) was used (Fig. 8c).

The changes in particle size and morphology observed as a result of changing the solution composition during Pd precipitation are attributed to the relative contribution of two competing nucleation mechanisms (homogeneous and heterogeneous). Homogeneous nucleation involves the heterolytic splitting of hydrogen by $PdCl_4^{2-}$ (17);

$$PdCl_4^{2-} + H_2 \rightleftarrows HPdCl_3^{2-} + H^+ + Cl^- \qquad (3)$$

heterogeneous nucleation on the other hand appears to involve the hymolytic splitting of hydrogen by chemisorption on Pd metal:

$$Pd + H_2 \rightleftarrows 2Pd - H \qquad (4)$$

The activated hydrogen species then ($HPdCl_3^{2-}$ or Pd - H) reduces $PdCl_4^{2-}$ to metal. It is evident from equation (3) that homogeneous nucleation is suppressed in the presence of high acid (H^+) and salt (Cl^-) concentrations, while at the same time heterogeneous nucleation remains unaffected. The action of

anthraquinone is to adsorb on the freshly formed Pd particles and activate the total surface of the metal thus facilitating the production of smooth particles.

PLATINUM

The precipitation kinetics of Pt from H_2PtCl_6 - HCl - NaCl media by hydrogen reduction were found to be fast but considerably slower than that of Pd. The effects of solution matrix (HCl/NaCl), hydrogen pressure, temperature, catalyst, and dissolved Pt(IV) concentration on precipitation kinetics are presented in Figs. 9-12. As it can be seen in Fig. 9 the higher the HCl and/or NaCl concentrations the slower the kinetics. Thus, while 1 hour is required for complete precipitation of Pt from a solution of 0.5 M HCl - 2M NaCl, only 5 min. is needed for precipitation from a solution of 0.1 M HCl - the other conditions being constant at 25°C, 50 psi H_2 and 1 g/l Pt(IV). An induction period is observed, which is more pronounced, when HCl and NaCl exceed the 1 M concentration level (Fig. 9) or a low hydrogen pressure (25 or 50 psi) is applied (Fig. 10). At the end of the induction period the metal precipitation rate becomes very fast.

This type of precipitation curve is characteristic of autocatalysis. In fact analysis of the data with the following autocatalytic model (28),

$$f = 1 - \exp(-kt^n)$$

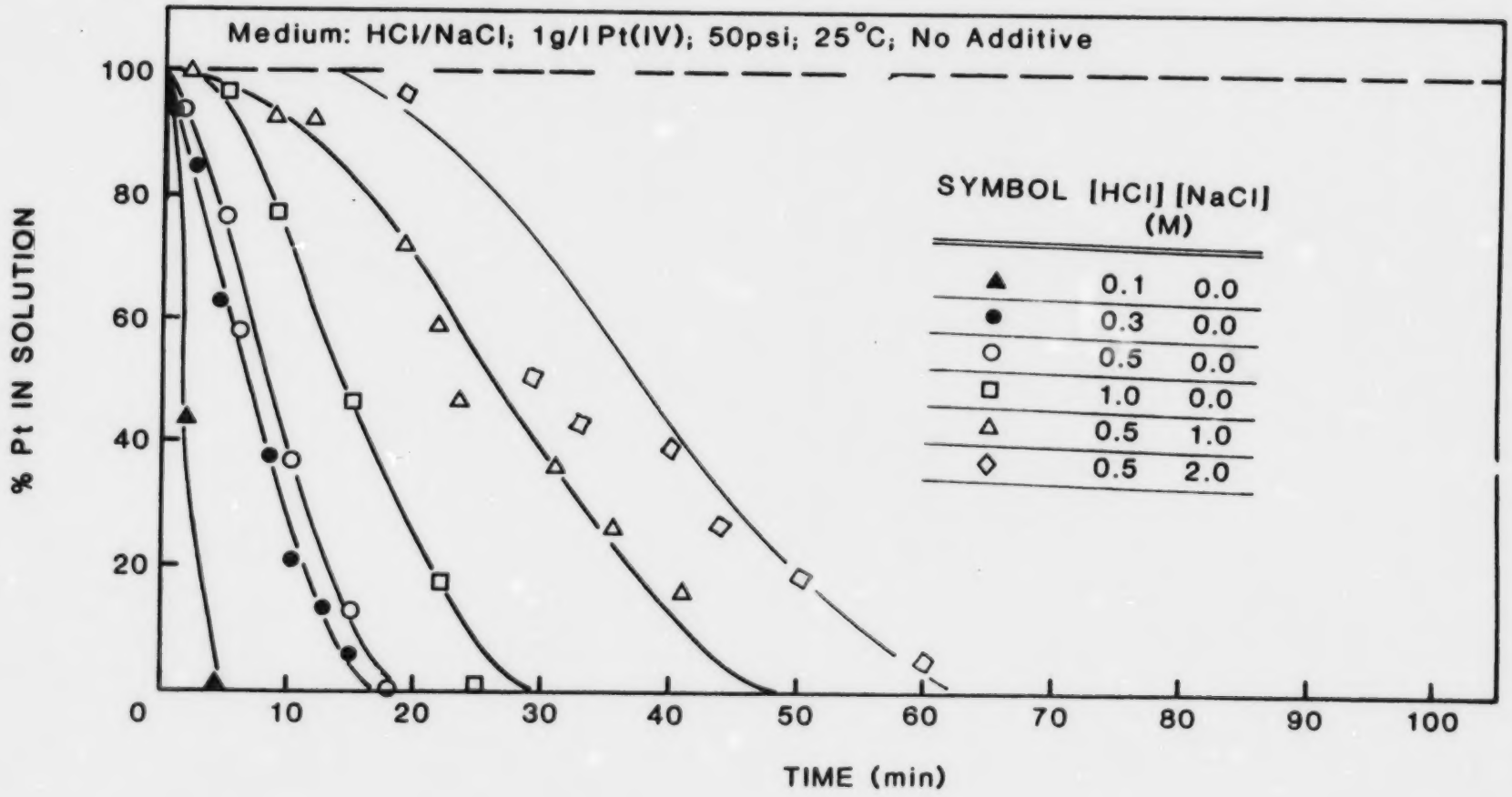


Fig. 9 Precipitation of Pt from chloride liquors by hydrogen reduction at various HCl and NaCl concentrations (25°C, 50 psi H_2, 1 g/l Pt(IV)).

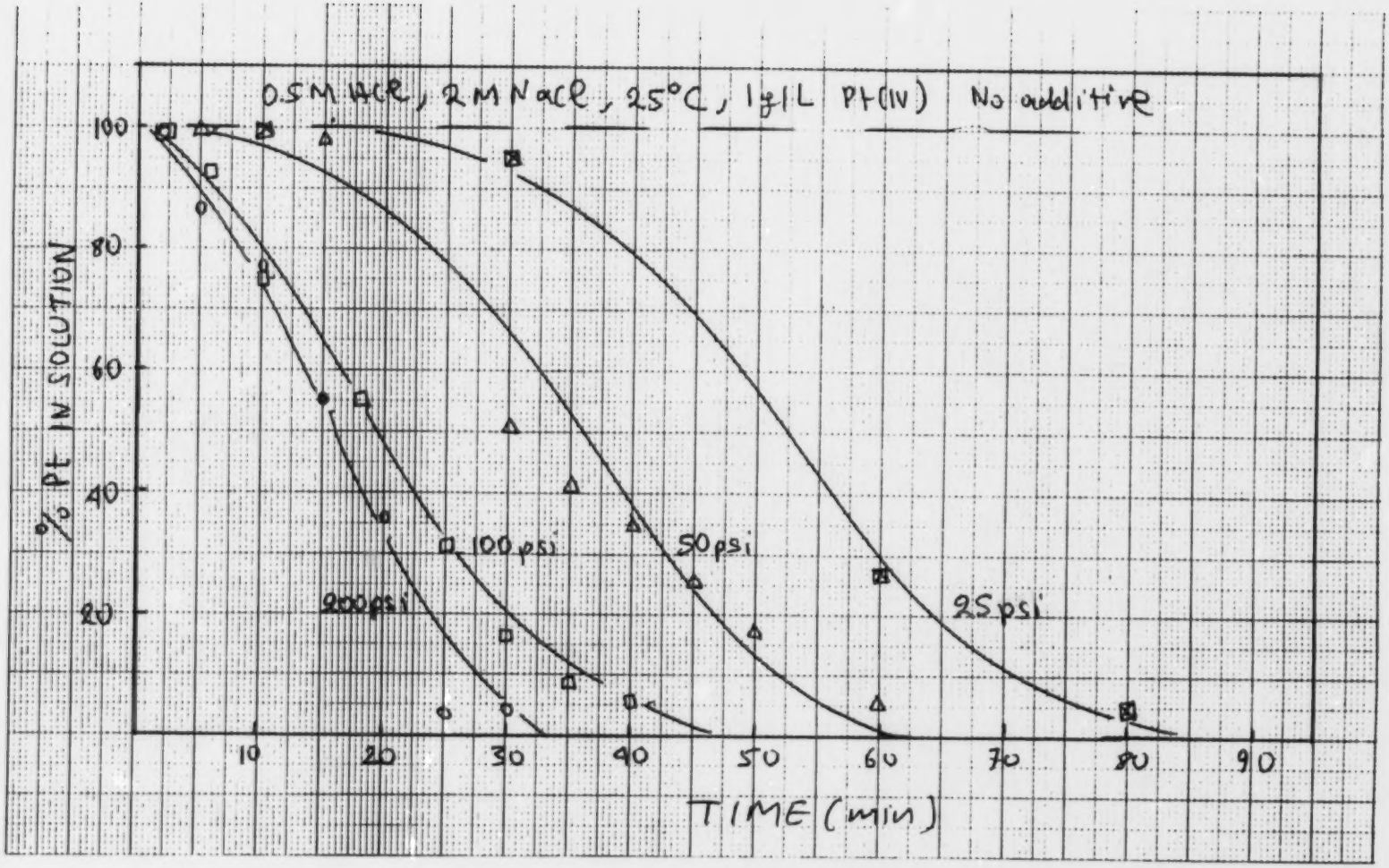


Fig. 10 Precipitation of Pt from chloride liquors by hydrogen reduction at various hydrogen pressures (25°C, 1 g/l Pt(IV), 0.5 M HCl, 2.0 M NaCl).

where f is the fraction of metal precipitated at time t, while k and n are nucleation and growth constants, showed good agreement with most of the experiments. The observed autocatalytic effect could be either due to the intermediate formation of Pt(II) or due to the actual Pt metal formation. The results of Fig. 11 demonstrate in fact that addition of Pt(II) as $PtCl_2$ or Pt metal as seed to the reduction solution produced faster kinetics and at the same time eliminated the induction period. Findlay (14) has shown that the true catalyst in this case is $PtCl_4^{2-}$. When Pt metal is used an equilibrium process generates $PtCl_4^{2-}$ (eq. 6); the equilibrium constant is 5 at 60°C (29):

$$Pt + PtCl_6^{2-} + 2Cl^- \rightleftarrows 2PtCl_4^{2-} \qquad (6)$$

The precipitation kinetics were also found to accelerate greatly be raising the temperature (Fig. 11) or using higher Pt(IV) concentrations (Fig. 12). These latter two effects are considered manifestations of a process controlled by homogeneous nucleation. The controlling step believed to be the initial formation (induction period) of a Pt(IV) hydride complex (eq. 7):

$$PtCl_6^{2-} + H_2 \rightleftarrows HPtCl_5^{2-} + H^+ + Cl^- \qquad (7)$$

$HPtCl_5^{2-}$ reduces then $PtCl_6^{2-}$ first to $PtCl_4^{2-}$ and finally to metal. The proposed mechanism accounts for the inhibition caused by H^+ and Cl^- (eq. 7) and the elimination of the induction period when $PtCl_2$ or Pt metal is used as catalyst.

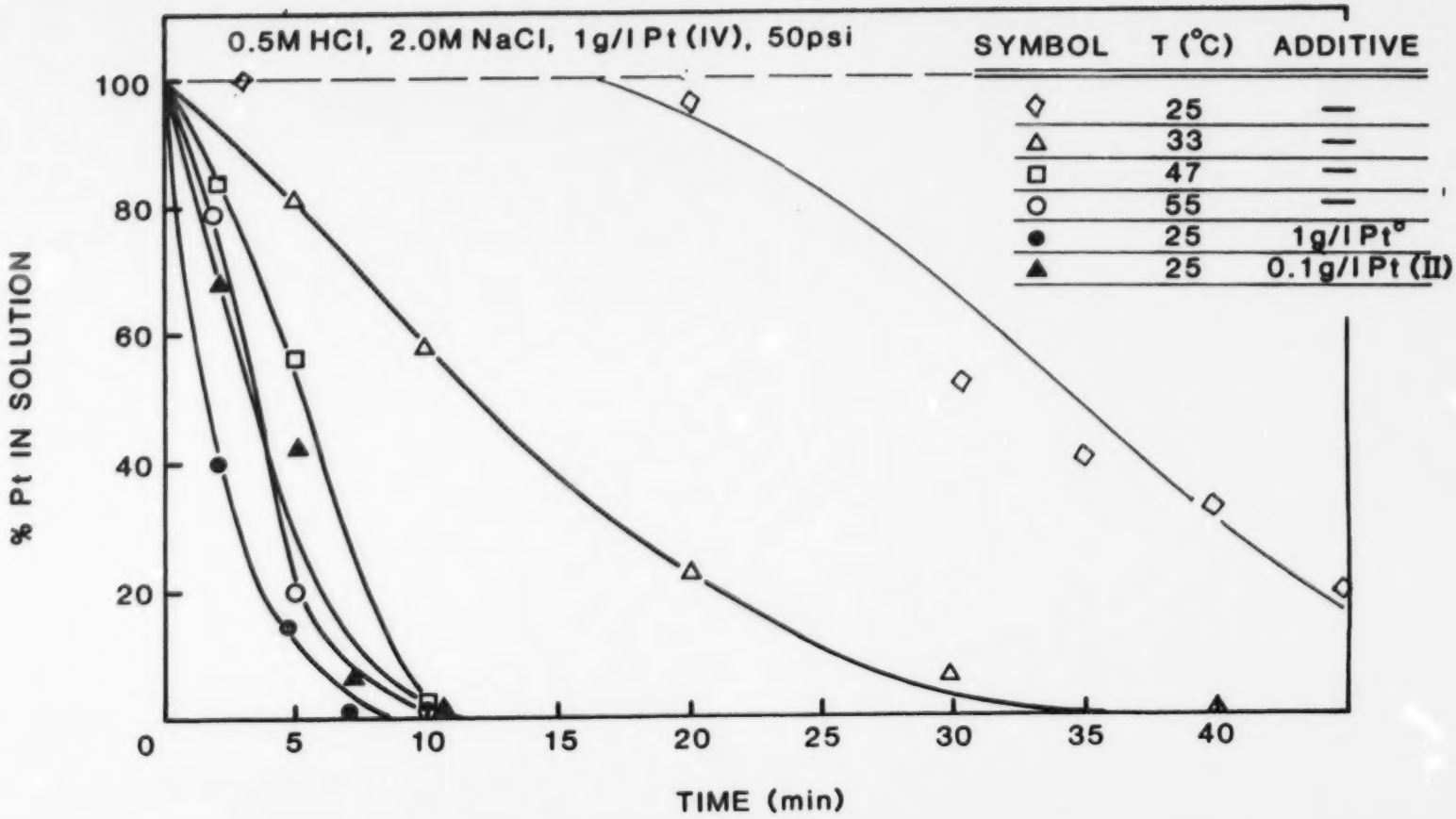


Fig. 11 Precipitation of Pt from chloride liquors by hydrogen reduction at various temperatures and catalyst additions (0.5 M HCl, 2.0 M NaCl, 1 g/l Pt(IV), 50 psi H_2).

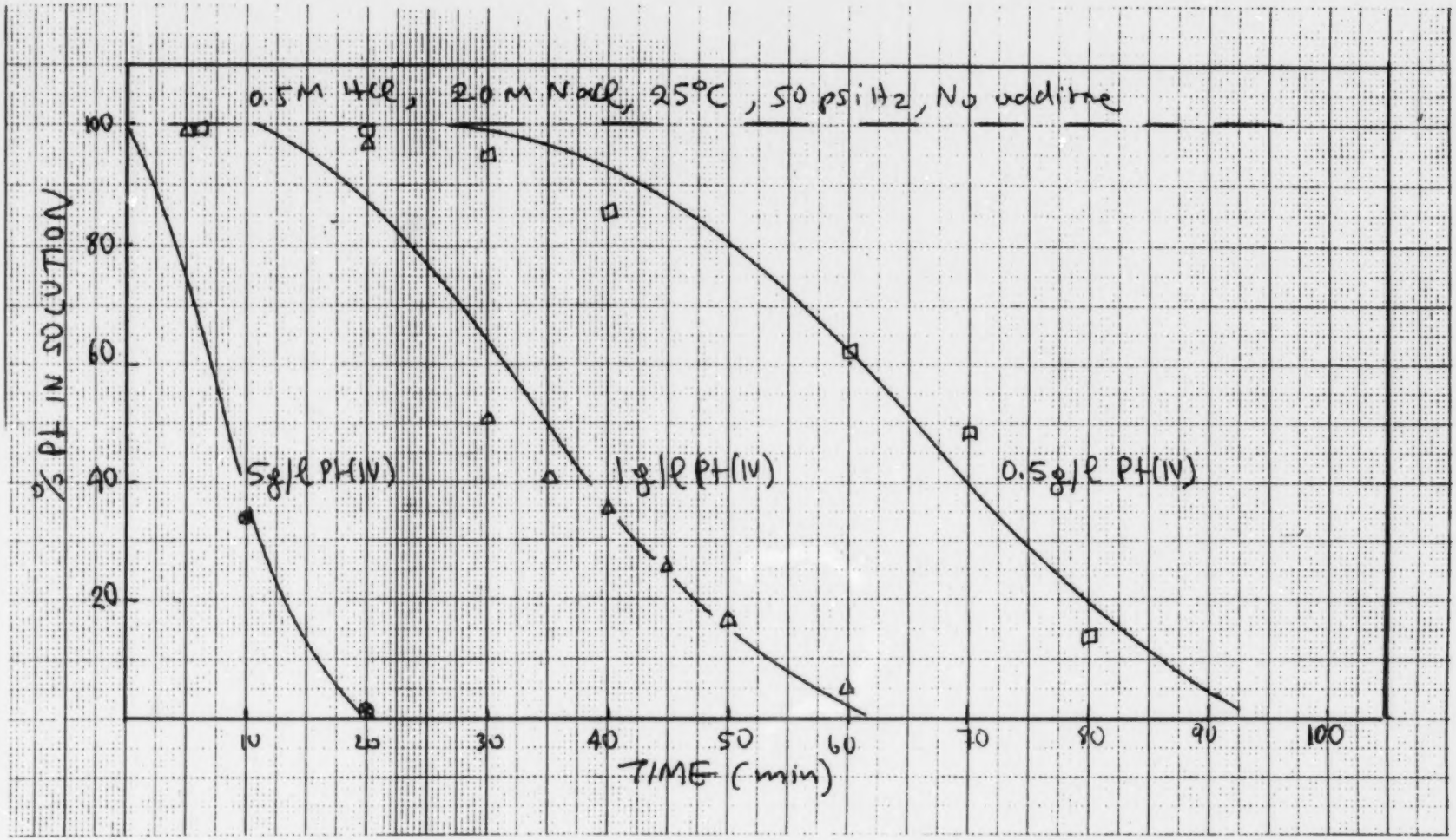
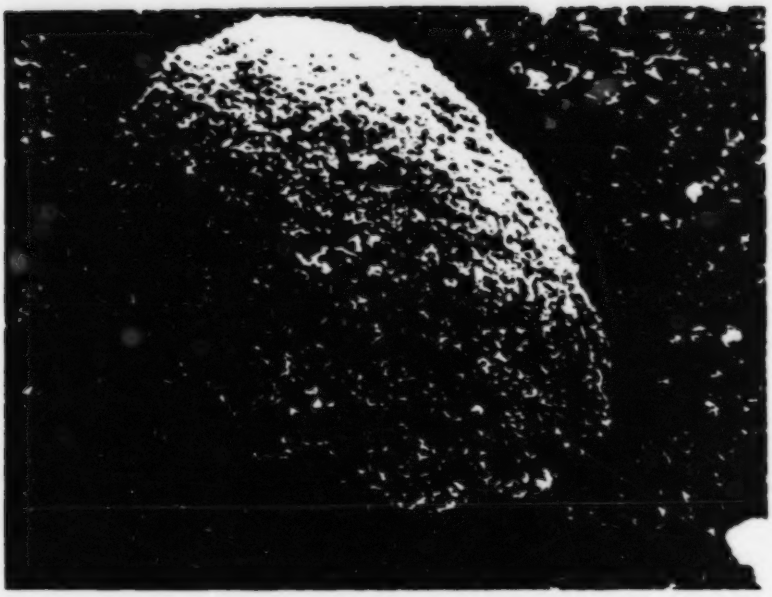


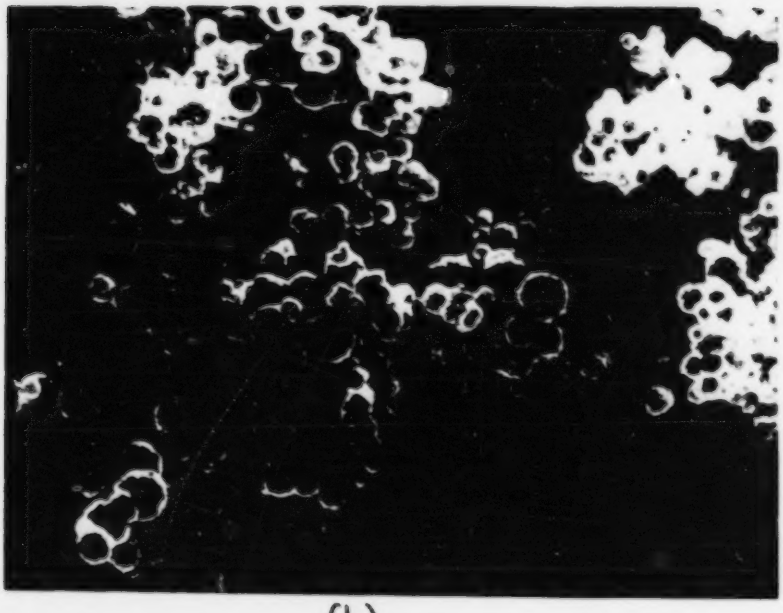
Fig. 12 Precipitation of Pt from chloride liquors by hydrogen reduction at various Pt(IV) concentrations (0.5 M HCl, 2.0 M NaCl, 25°C, 50 psi H_2).

The bulk of the metal was found to precipitate as black powder while the rest was loosely adhered on the walls of the autoclave in the form of large leaflets with lustrous appearance (Fig. 13a). By focussing on the big lump of Fig. 13a the picture shown in Fig. 13b was obtained. As can be seen, the primary Pt particles are smooth and spherical with most of them having a diameter in the range of 0.5 - 1.0 μm. The powder of Fig. 13 (a,b) was produced from a 0.5 M HCl - 2.0 M NaCl solution. The primary Pt particles were considerably more uniform and finer (∿ 0.2 μm) when the reduction was catalysed by the addition of Pt(0) or Pt(II). Identical morphologies in both cases were obtained (Figs. 14 and 15). The latter observation is in support of the presumed catalytic roles of Pt(II) and Pt(0) discussed above.

Aggregation of the extremely fine particles was observed but it appeared to be rather loose. The same does not appear to be true however for the Pt powders precipitated from NaCl-free solutions. In this case the produced aggregates consisted of solidly bonded together particles (Fig. 16a,b). It seems then that under these conditions reaction (6) is not shifted to the right (due to lack of high Cl^- concentration) and thus Pt metal does not convert any more to $PtCl_4^{2-}$ but rather acts directly as a hydrogenation catalyst (heterogeneous nucleation). The simultaneous operation of both homogeneous and heterogeneous nucleation has therefore to be avoided if production of fine monodisperse particles is sought.



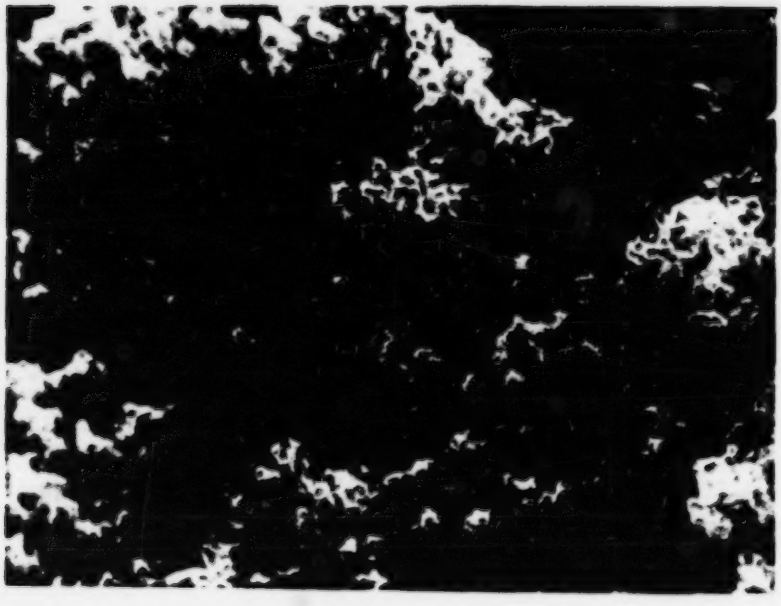
(a)



(b)

Fig. 13 Platinum powders precipitated from 0.5 M HCl/2.0 M NaCl solution by hydrogen reduction (25°C, 50 psi H_2, 1 g/l Pt(IV)).

(a)



(b)

Fig. 14 Platinum powders produced in the presence of recycled platinum seed (conditions same as in Fig. 13).

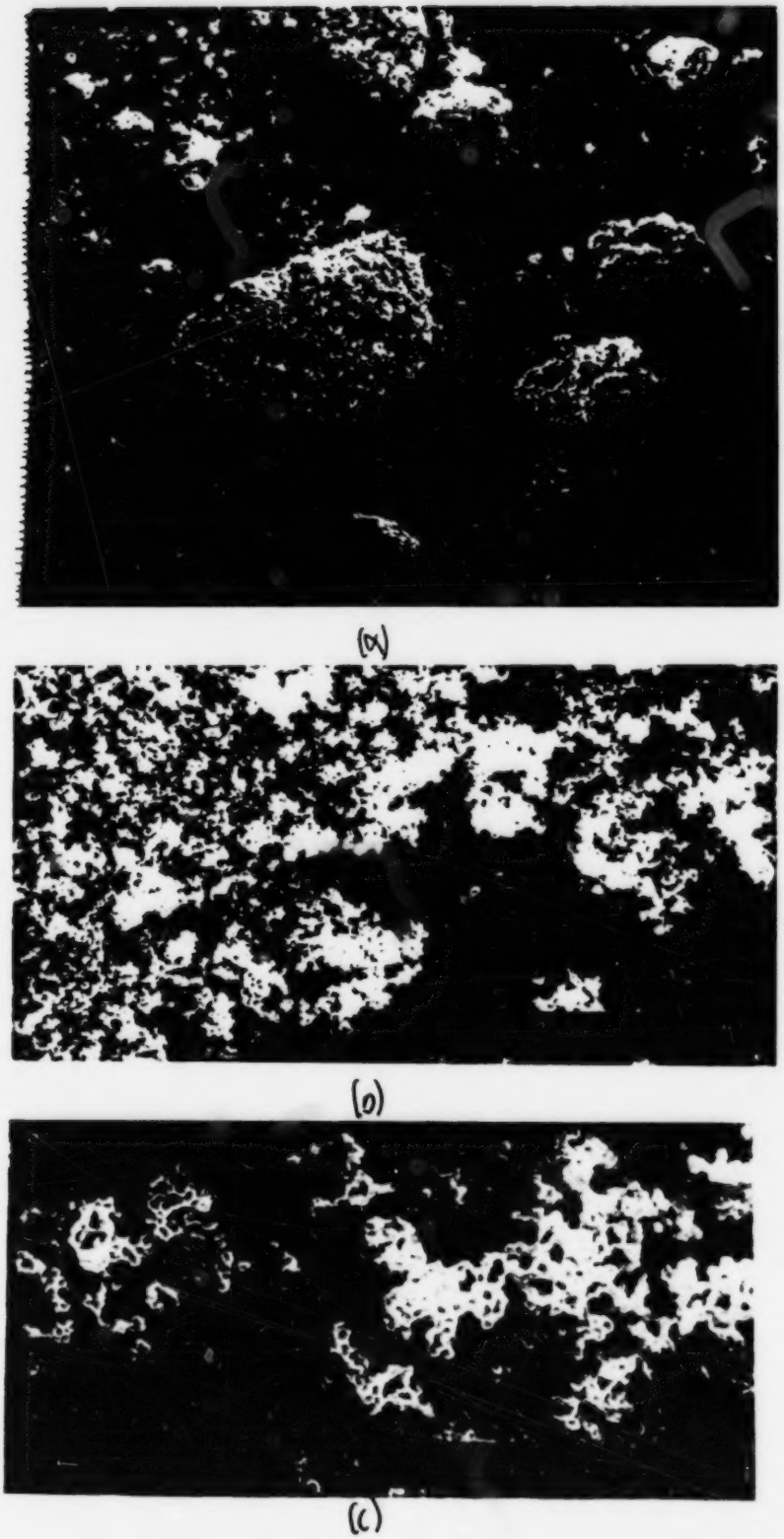
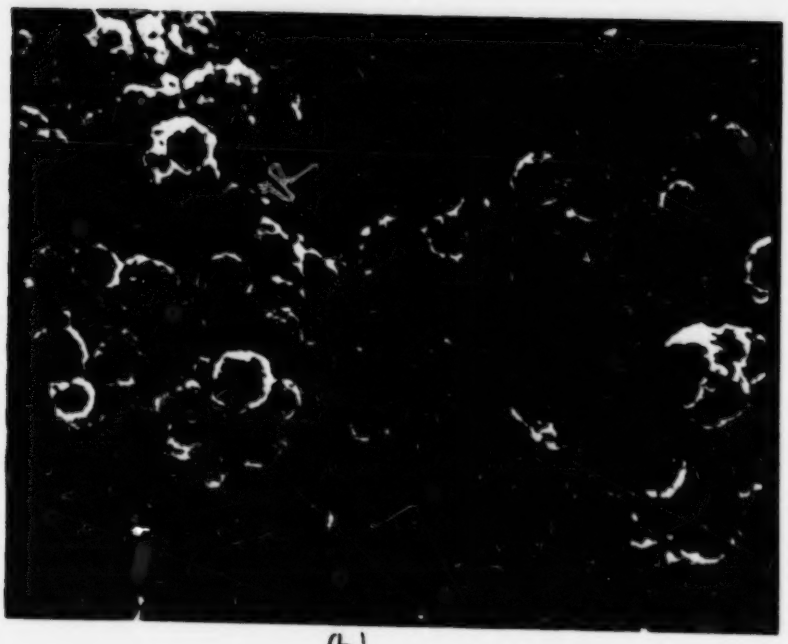


Fig. 15 Platinum powders produced in the presence of 100 ppm $PtCl_2$ (conditions same as in Fig. 13).

(a)



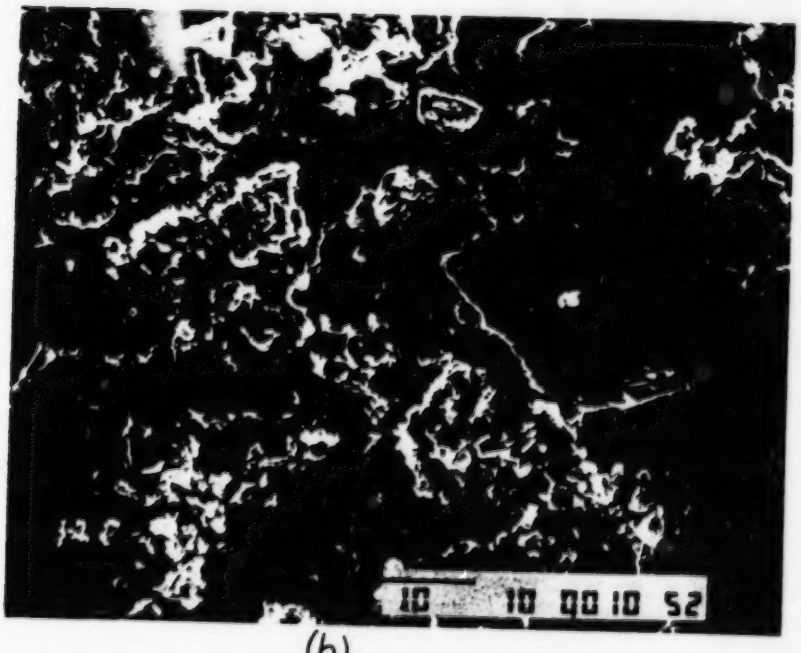
(b)

Fig. 16 Platinum powders cemented together - precipitation from a 0.5 M HCl solution (25°C, 50 psi H_2, 1 g/l Pt(IV)).

Addition of some surface active molecules in the precipitation system resulted in markedly different platinum morphologies. Anthraquinone additions (0.5 g/l) had as a result the total elimination of the spherical particle morphology and instead the production of mostly flakes (Fig. 17a) and platelets (Fig. 17b). Also, alizarin, which has a similar structure to that of anthraquinone, both carry two carbonyl groups $\geq C = 0$ (30), gave the same flake-type morphology. However, dextrin, which carries both hydroxyl and carbonyl groups(30) gave the morphology of Fig. 18. The primary Pt particles are seen to be relatively uniform with rough surface and $\sim$ 0.5 μm diameter. Finally, when Pt was precipitated directly from the strip liquor following solvent extraction and stripping with H_2O (Fig. 1b), completely smooth spherical particles were produced (Fig. 19). Apparently upon stripping traces of the organic solvent (Lix 26 - isodecanol-Solvesso 150) were transferred in the aqueous phase and affected thus the morphology of the precipitated metal powder. It is postulated at this point that isodecanol is the principal organic substance responsible for the observed improvement in particle morphology. This is an important observation which makes the recovery of Pt from the strip liquor by H_2 recovery even more attractive.

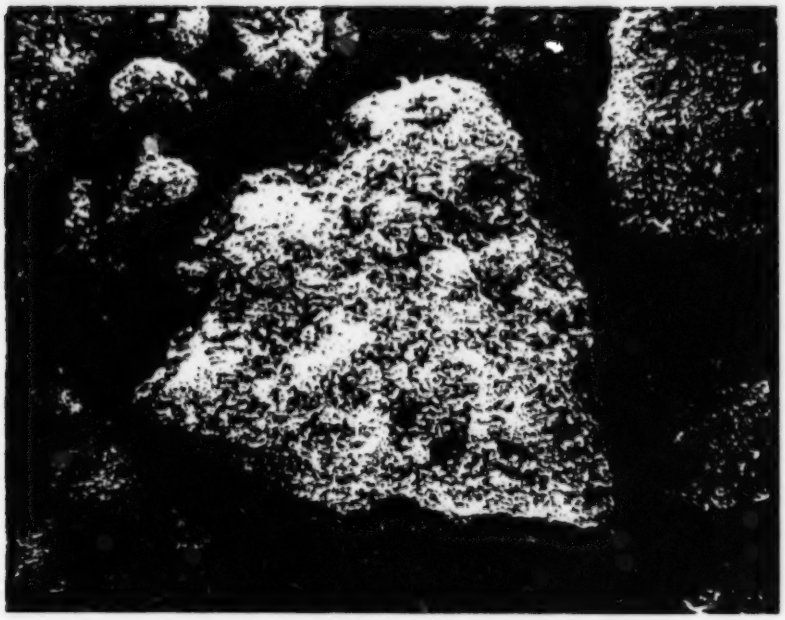
Apparently, adsorption of the organic molecules on the surfaces of freshly formed metal nuclei controls the particle size of the metal powders. The nature of the polar

(a)

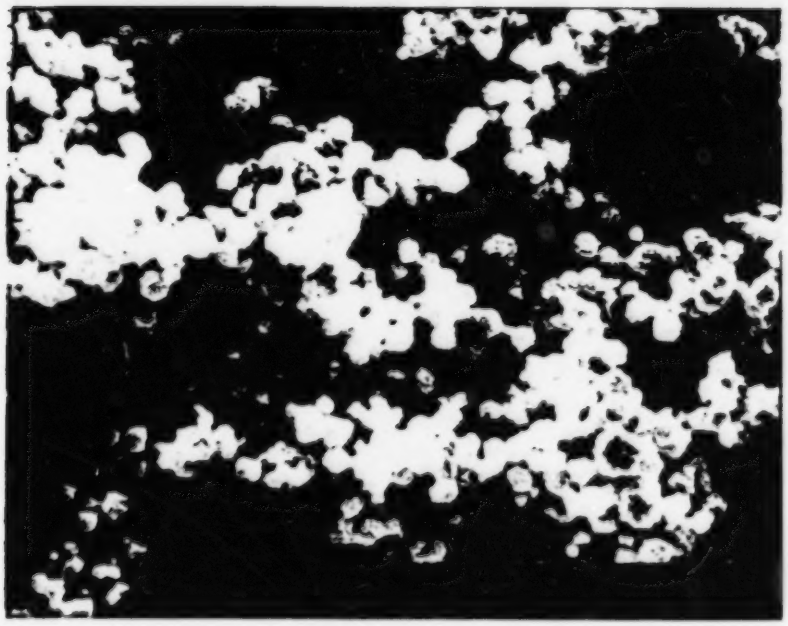


(b)

Fig. 17 Platinum powders produced in the presence of 0.5 g/l anthraquinone (1 g/l Pt(IV), 0.2 M HCl, 60°C, 100 psi H_2).



(a)



(b)

Fig. 18 Platinum powders produced in the presence of 0.5 g/l dextrin (conditions same as in Fig. 17).

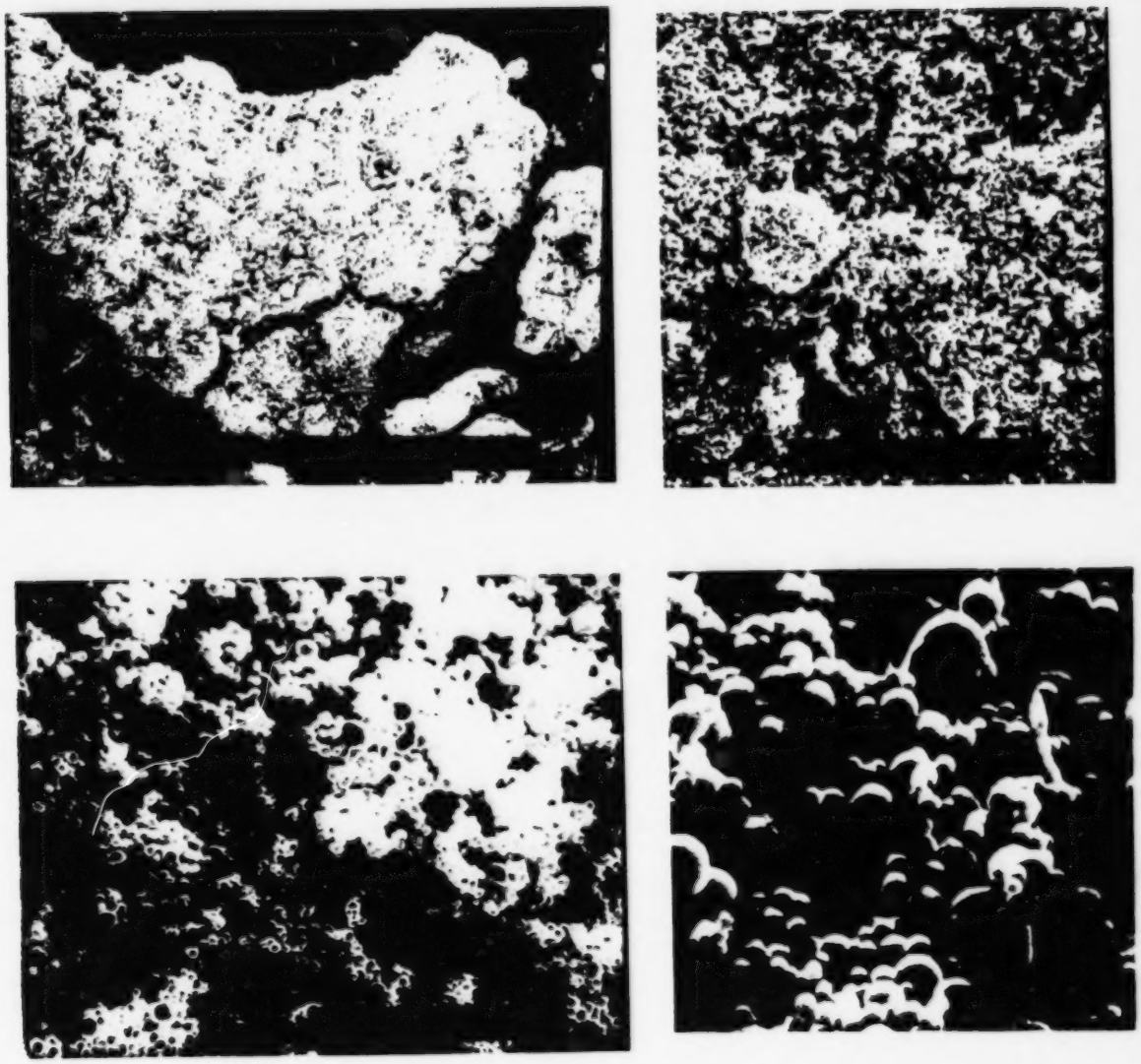


Fig. 19 Platinum powders produced directly from the Pt strip liquor (0.2 N HCl + traces of organic solvent) (other conditions same as in Fig. 17).

group (-OH vs $\geq$C=0) of the surface active molecules seems therefore to have a direct effect on the powder morphology obtained. Further work is needed to optimize the use of organic additives in the precipitation mixture as a means of preventing aggregation (or coagulation) of the fine particles. Aggregation is the overall net effect of colloidal forces acting on the particles. Van der Waals attraction forces are responsible for coagulation while electrostatic repulsion forces arising from the electric double layers surrounding the particles act against coagulation. Strengthening the electrostatic repulsion forces by either adjusting the ionic strength of the solution or the surface potential of the particles via specific ion adsorption are avenues colloid chemists use to prevent coagulation (31). From the two avenues, the latter appears to be the most effective especially when surfactants are used (32). Depending on the orientation of the surfactant molecules adsorbed on the particles coagulation (parallel orientation) or dispersion (perpendicular orientation) occurs. In the light of these phenomena, the action of anthraquinone-alizarin (parallel orientation) and dextrin-isodecanol (perpendicular orientation) on the Pt powder morphology obtained can be explained. Moreover long-chain organic molecules absorbed with perpendicular orientation give rise to further prevention of coagulation-aggregation via steric stabilization (33). Aggregation of the fine primary particles is in general reversible (34), i.e. predispersion of the particles is possible, provided though that the aggregates have not been cemented via heterogeneous nucleation (Fig. 16).

PART B: BINARY METAL SOLUTIONS

The results of part A showed recovery of Pt and Pd in a powder form from purified strip liquors originating from the solvent extraction process flowsheet of Fig. 1b to be technically feasible and very attractive. The next step was to investigate the selectivity of the H_2 precipitation process vis-a-vis several metal impurities that could be encountered in platinum refining solutions. The experimental procedure involved heating 400 ml of metal-bearing solution (250 ppm PM; 1000 or 500 ppm BM and 0.5 M HCl) in a glass reaction kettle to 60°C and flushing the kettle continuously with H_2. H_2 was sparged under the stirring impeller for better gas distribution.

Fe(III) Binary Solutions

Pd(II)/Fe(III) precipitation curves are shown in Fig. 20. No significant change in Fe concentration was observed during the 2 hour reduction test (Fig. 20a) while an hysteresis of just over 60 min. was observed in Pd precipitation. Pd was recovered in a powder form and no plating was observed. According to the single metal experiments and the applied conditions complete Pd precipitation in less than 3 min. would have to be expected (Fig. 7, p. 18). The observed hysteresis in the present binary metal system has to be attributed to the preference of $PdCl_4^{2-}$ to act as a homogeneous catalyst facilitating the reduction of Fe(III) to Fe(II) first before it undergoes reduction itself (17).

FIGURE 20a [Pd] vs. reaction time for Fe-Pd tests

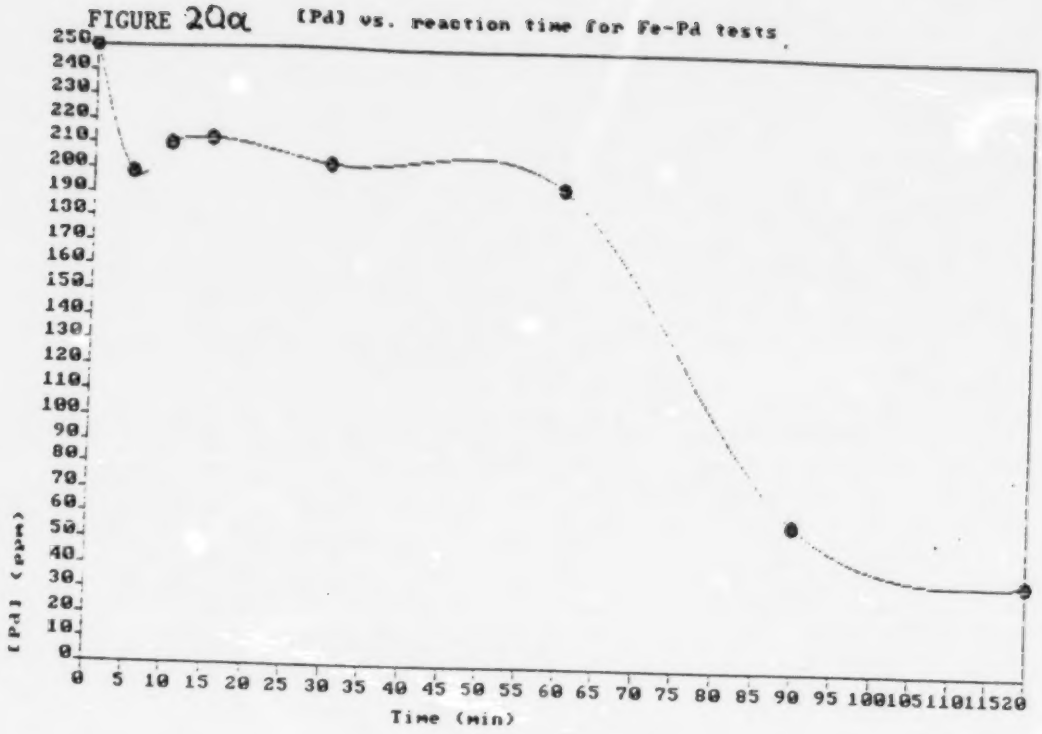


FIGURE 20b [Fe] vs. reaction time for Fe-Pd tests

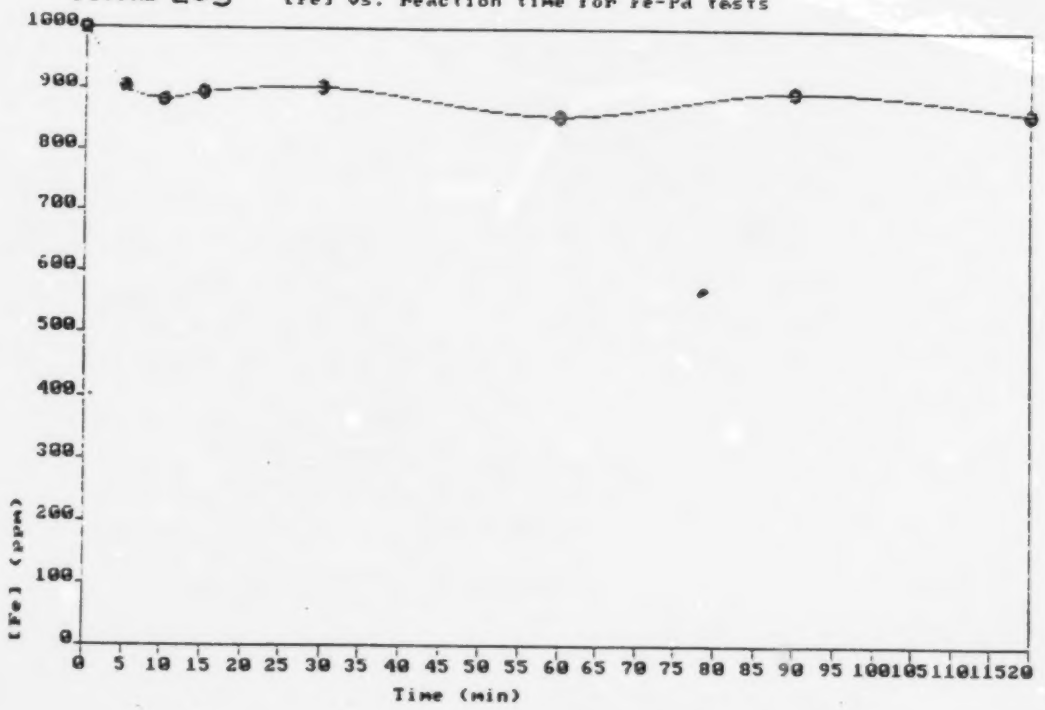


Fig. 20 Hydrogen reduction of a Pd(II)/Fe(III) binary chloride solution (0.5 M HCl, 60°C, 15 psi H_2).

FIGURE 21a [Pt] vs. reaction time for Fe-Pt tests

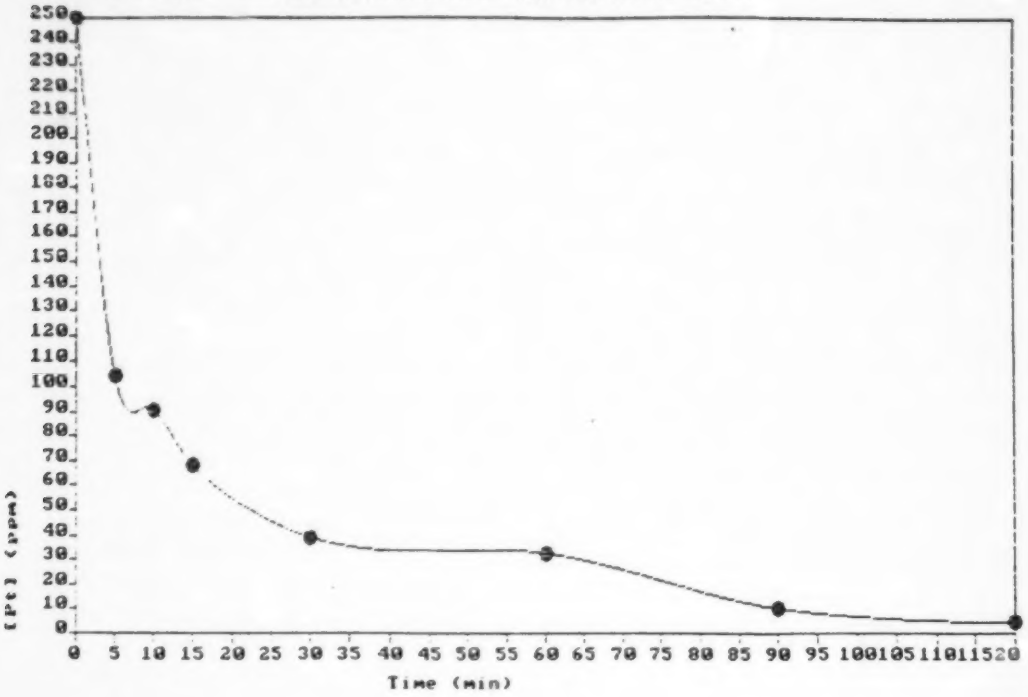


FIGURE 21b [Fe] vs. reaction time for Fe-Pt tests

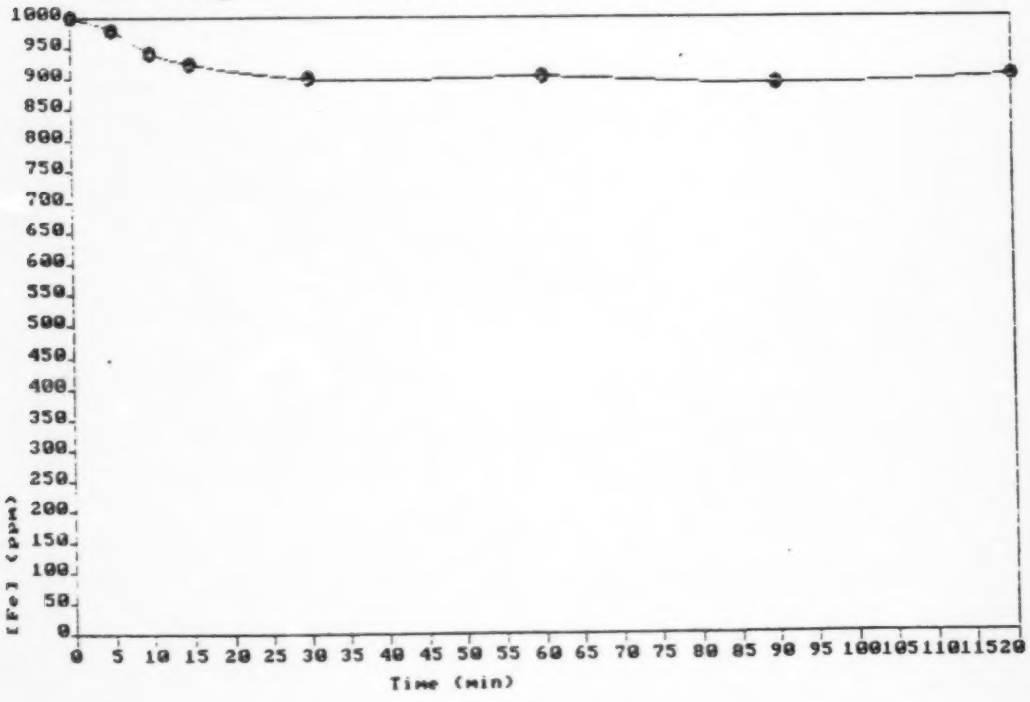


Fig. 21 Hydrogen reduction of a Pt(IV)/Fe(III) binary chloride solution (conditions same as in Fig. 20).

The respective reduction curves for the system Pt(IV)/Fe(III) are shown in Fig. 21. No hysteresis in Pt precipitation is observed now while Fe concentration again seems to remain unaffected after 2 hours of reduction. Platinum was recovered mostly as powder with no significant plating observed to occur. It appears then Pt(IV) not to exhibit similar preference like Pd(II), Rh(III) or Ru(III) in catalysing first the reduction of Fe(III) to Fe(III) and after undergoing reduction itself (17,18,19).

Sb(III) Binary Solutions

The results obtained are illustrated in Fig. 22 (Pd(II)/Sb(III) and Fig. 23 (Pt(IV)/Sb(III)). No selective precipitation was possible. Sb precipitation apparently is catalysed by the presence of the dissolved precious metals. Reactor wall plating was not observed.

Bi(III) Binary Solutions

The respective curves (Figs. 24 and 25) showed that approximately 40% of the Bi precipitated out before Pd and Pt could be reduced. Again no selectivity is exhibited. Wall and agitator plating was observed.

As(III) Binary Solutions

The As-Pd results (Fig. 26) show that arsenic underwent complete precipitation in less than 5 minutes and then reduction

FIGURE 22a [Pd] vs reaction time for Sb-Pd tests

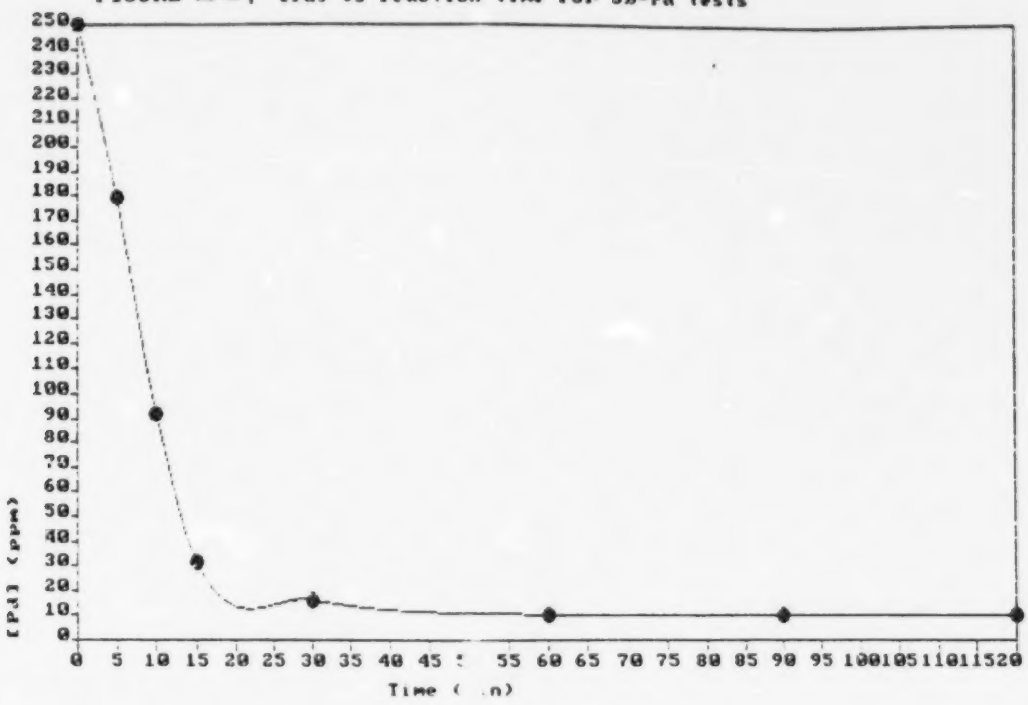


FIGURE 22b [Sb] vs reaction times for Sb-Pd tests

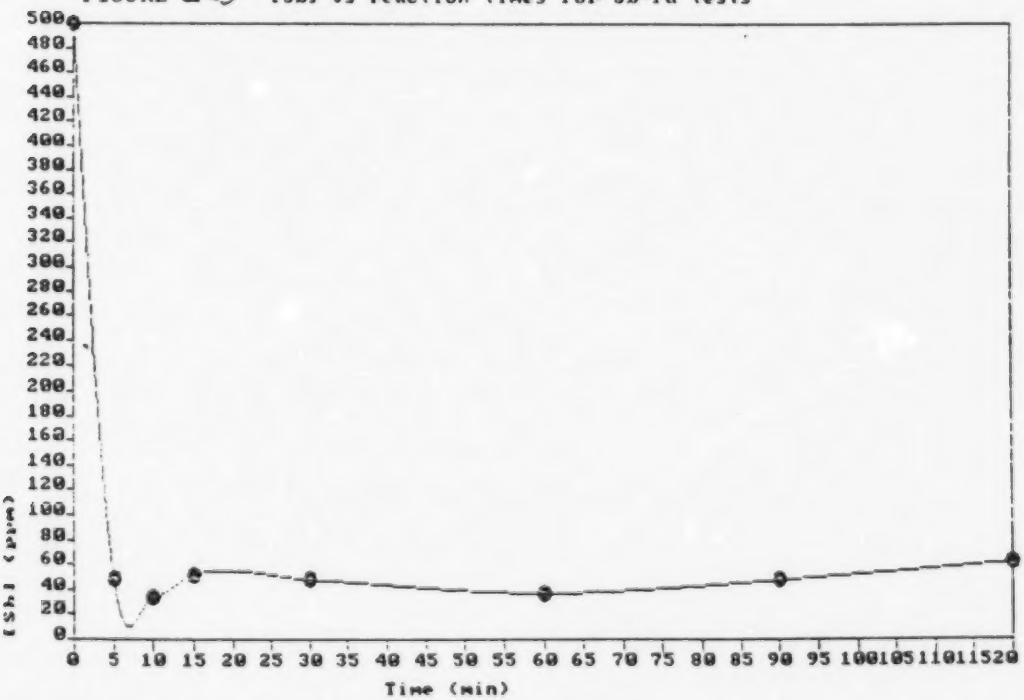


Fig. 22 Hydrogen reduction of a Pd(II)/Sb(III) binary solution.

FIGURE 23a [Pt] vs. reaction time for Sb-Pt tests

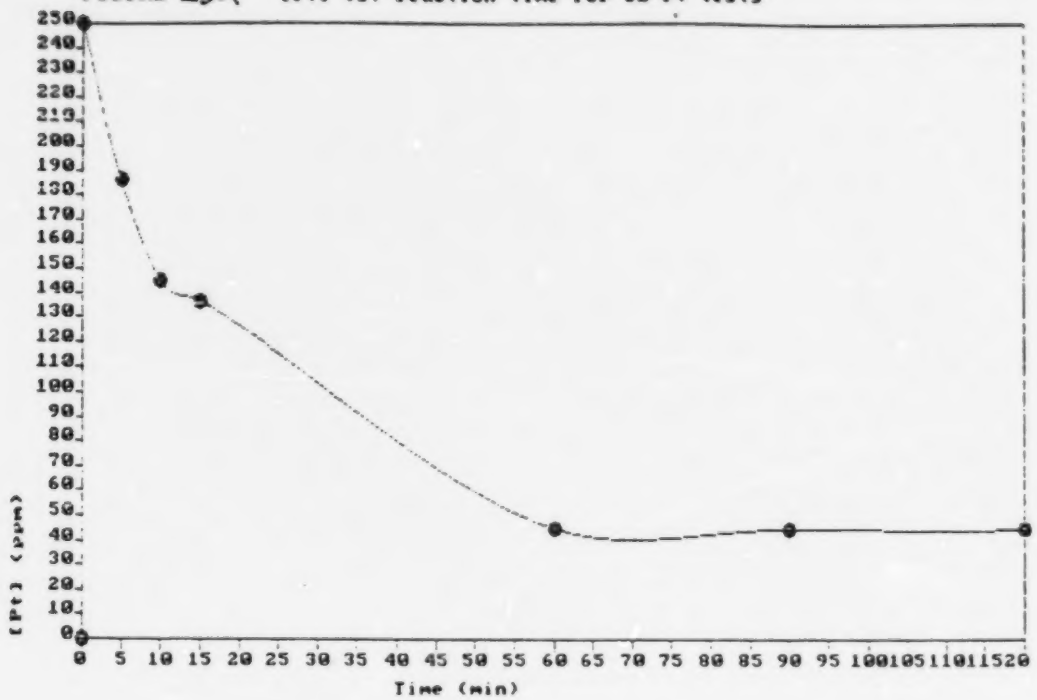


FIGURE 23b [Sb] vs reaction time for Sb-Pt tests

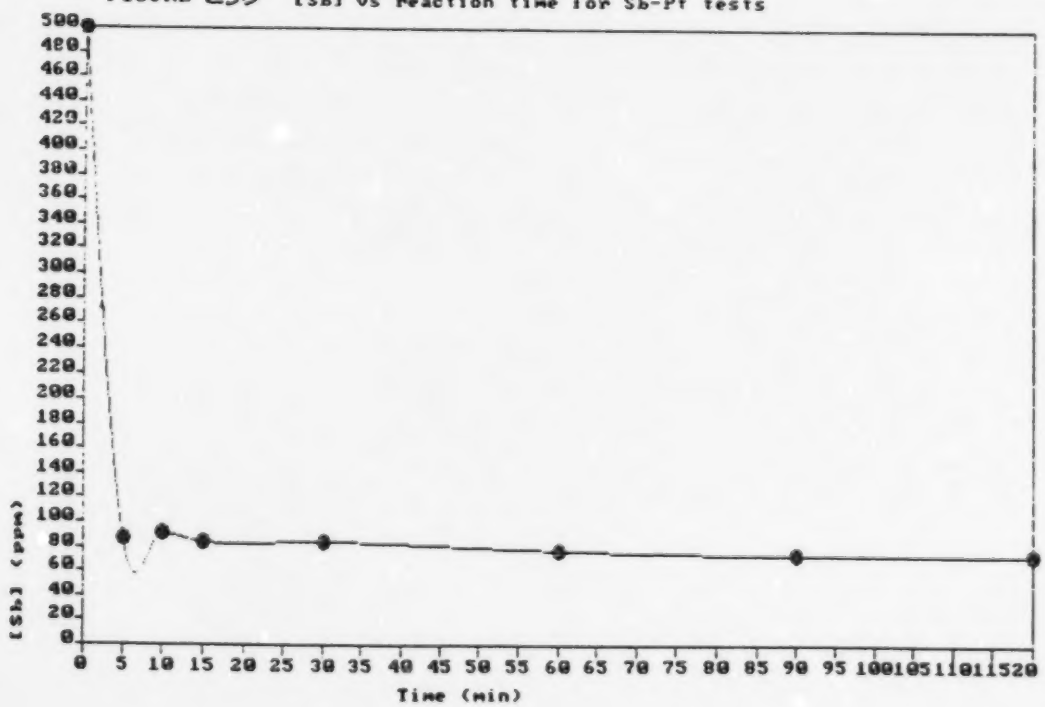


Fig. 23 Hydrogen reduction of a Pt(IV)/Sb(III) binary solution.

FIGURE 24a [Pd] vs reaction time for Bi-Pd tests

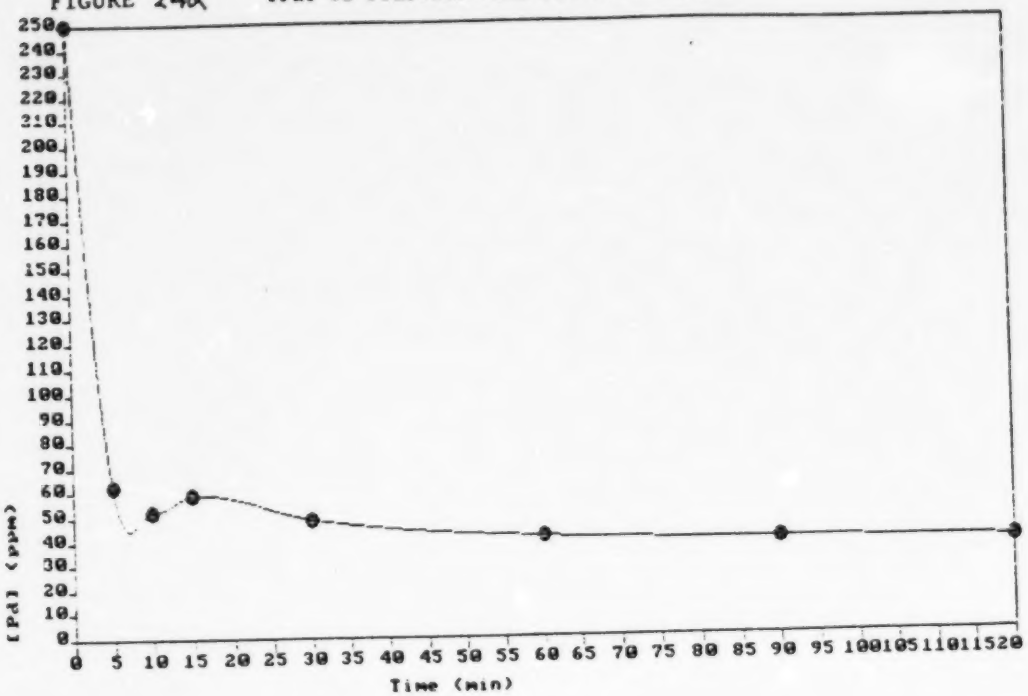


FIGURE 24b [Bi] vs reaction time for Bi-Pd tests

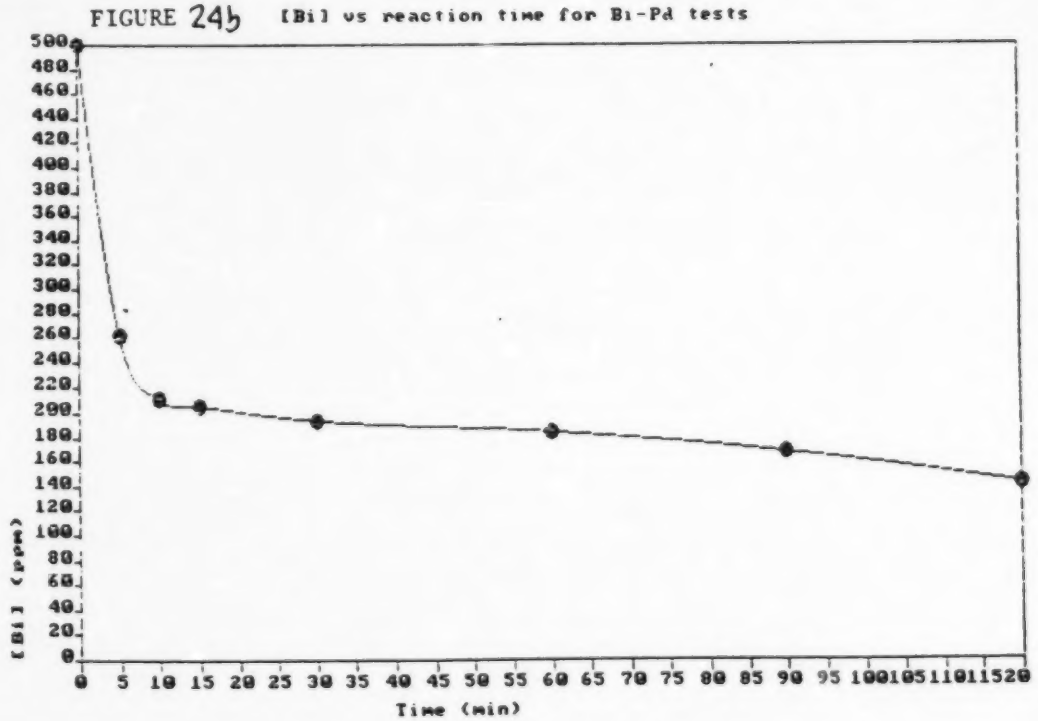


Fig. 24 Hydrogen reduction of a Pd(II)/Bi(III) binary solution.

FIGURE 25a [Pt] vs reaction time for Bi-Pt tests

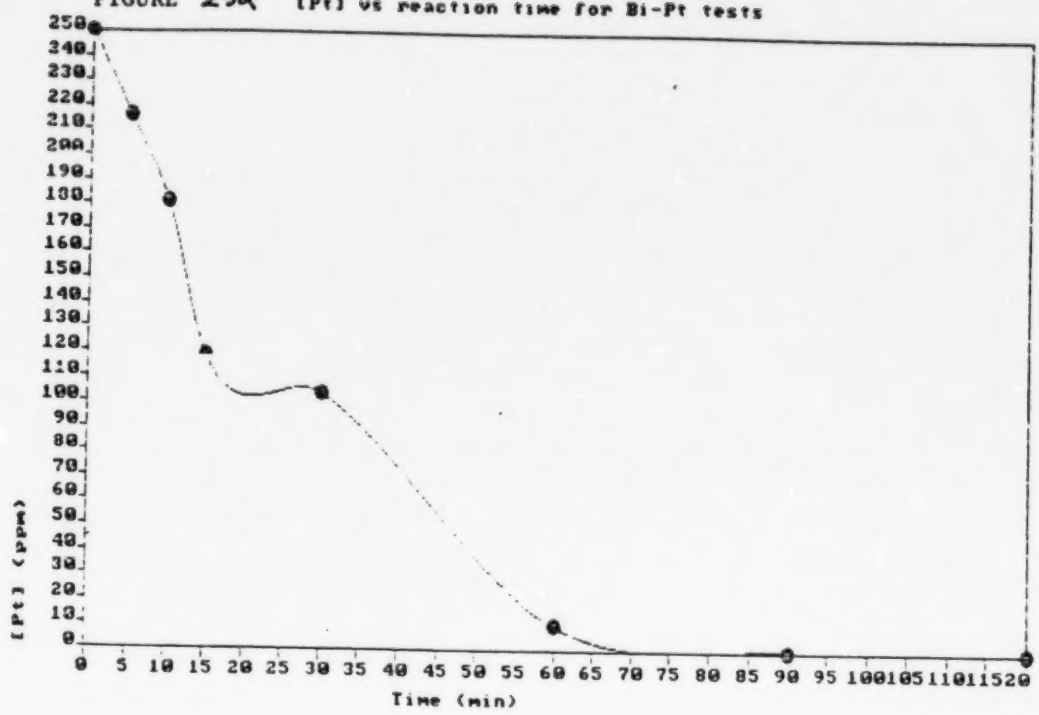


FIGURE 25b [Bi] vs reaction time for Bi-Pt tests

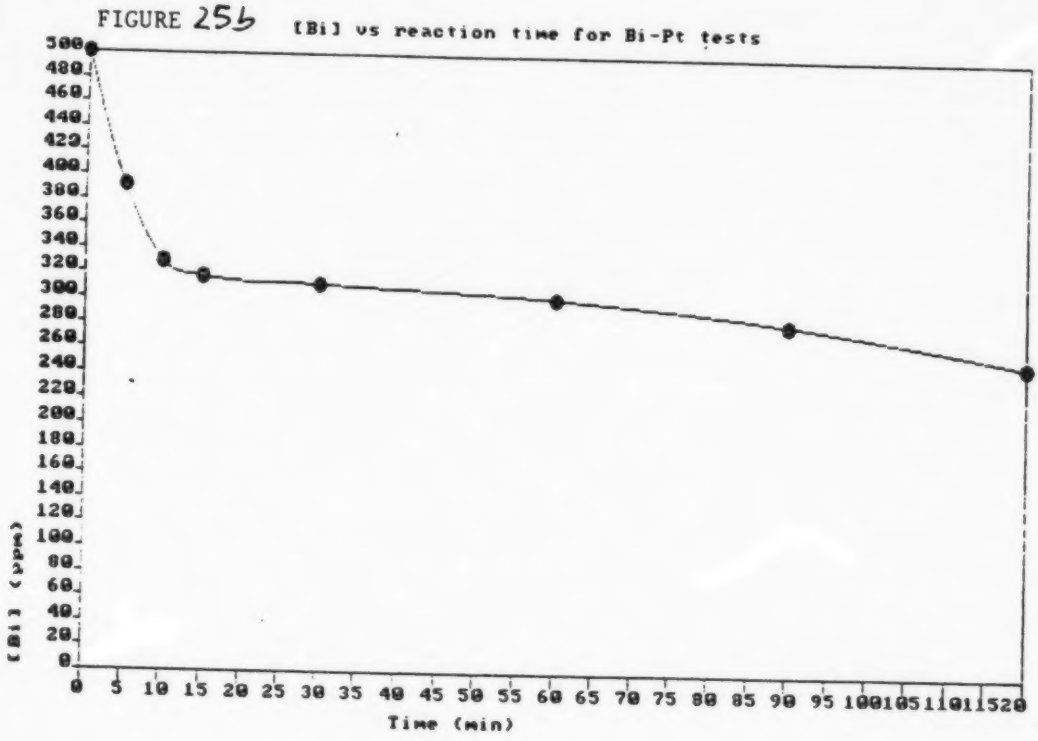


Fig. 25 Hydrogen reduction of a Pt(IV)/Bi(III) binary solution.

of Pd followed. The precipitation kinetics was somewhat slower in the case of As-Pt (Fig. 27) but again no selectivity was observed. The metal product was in extremely fine powder form. Filtration was difficult. No plating was observed.

Cu(II) Binary Solutions

The kinetics of the precious metal reduction were relatively slower than in other systems (Figs. 28 and 29). The copper precipitated out of the solution ahead of the precious metals but only to the extent of 50%, the rest remained in solution. This effect is similar to that of Bi. Selectivity was not achieved here either. In these experiments two important observations were made; (1) the precious metals plated the reactor walls and (2) the solution was black by the end of the experiment. This was probably due to a cupric to cuprous reduction step.

Pb(II) Binary Solutions

The Pb-Pd/Pb-Pt experiments also showed no selectivity (Figs. 30 and 31). 40% of the Pb precipitated out before the precious metal. The kinetics, as in all the binary metal experiments, were relatively slower than the respective single precious metal solutions. Plating was observed on the walls. The color of the final solution was grey due apparently to a fine Pb particle suspension.

FIGURE 26a [Pd] vs reaction time for As-Pd tests

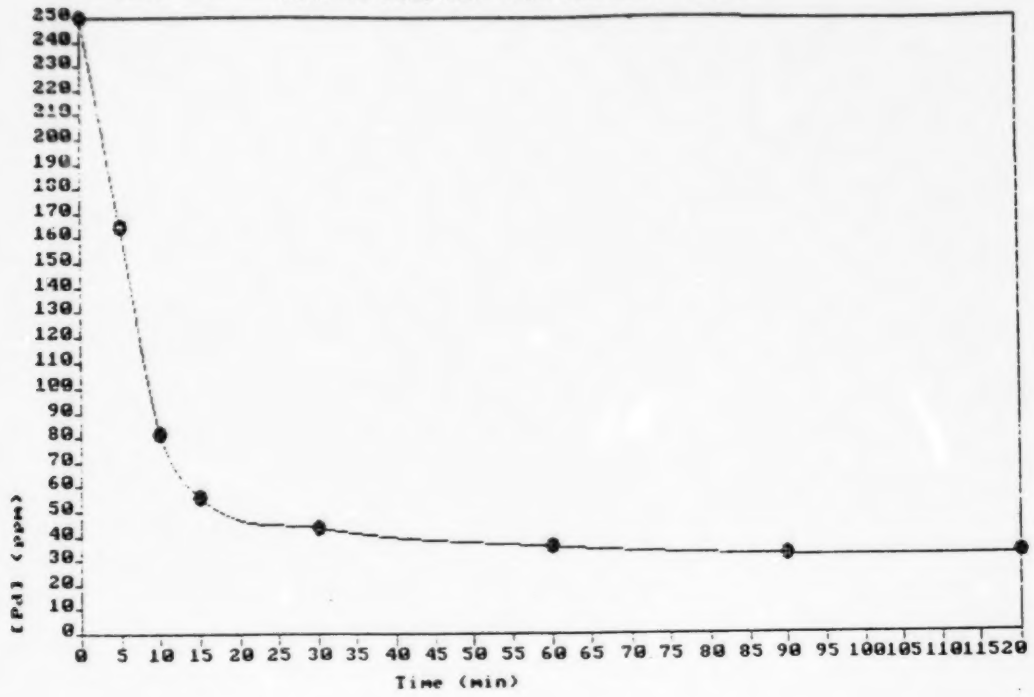


FIGURE 26b [As] vs. reaction time for As-Pd tests

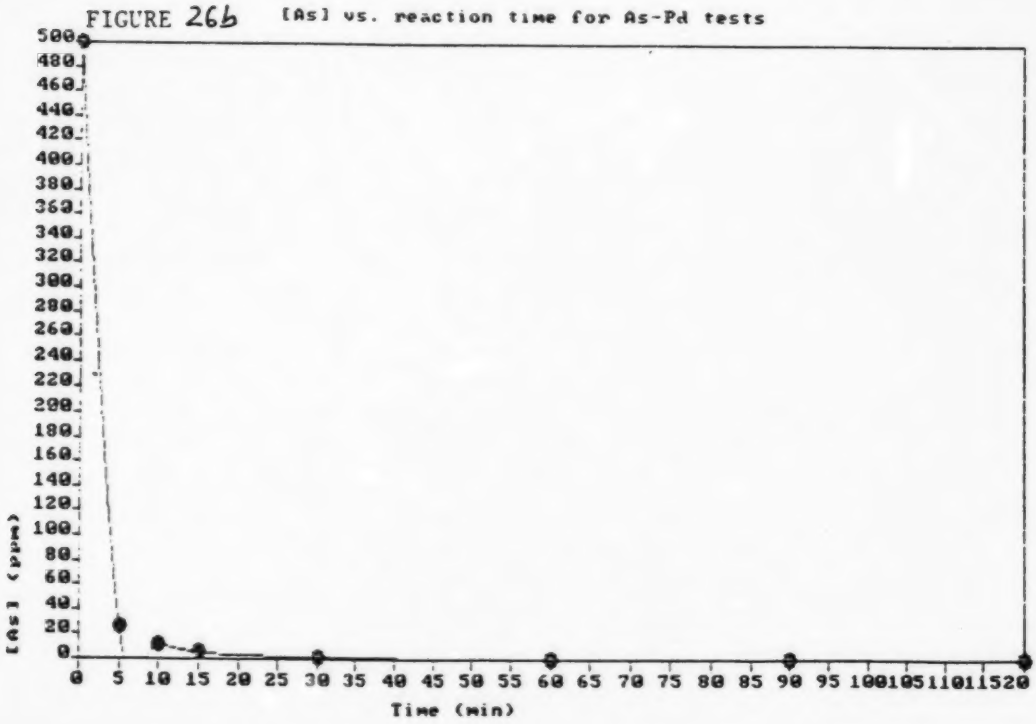


Fig. 26 Hydrogen reduction of a Pd(II)/As(III) binary solution.

FIGURE 27a

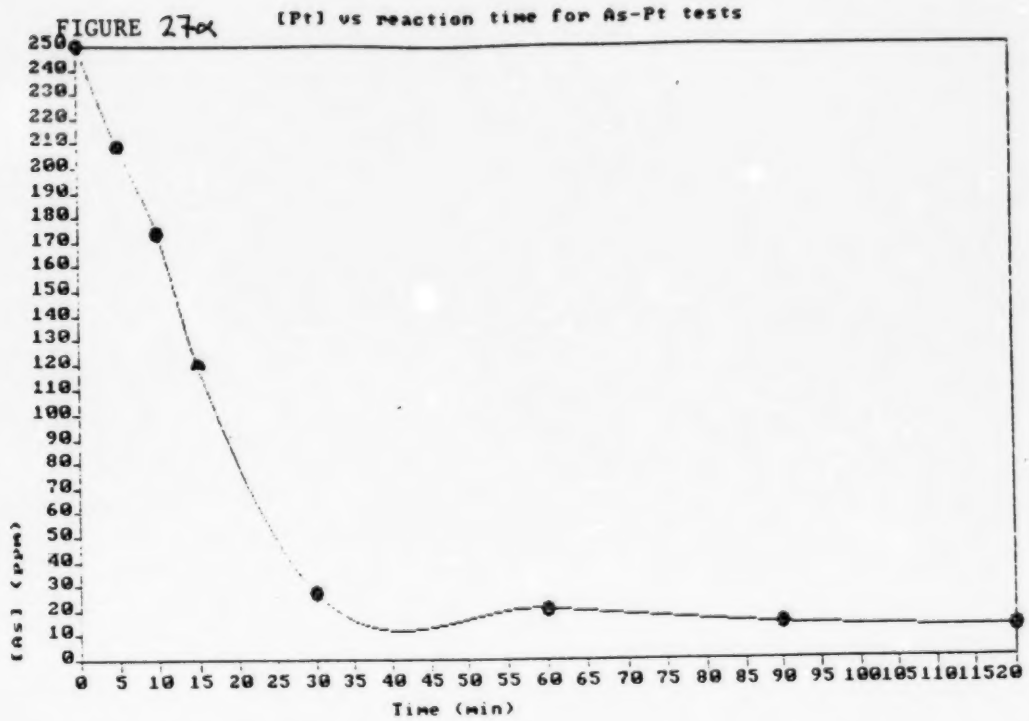


FIGURE 27b

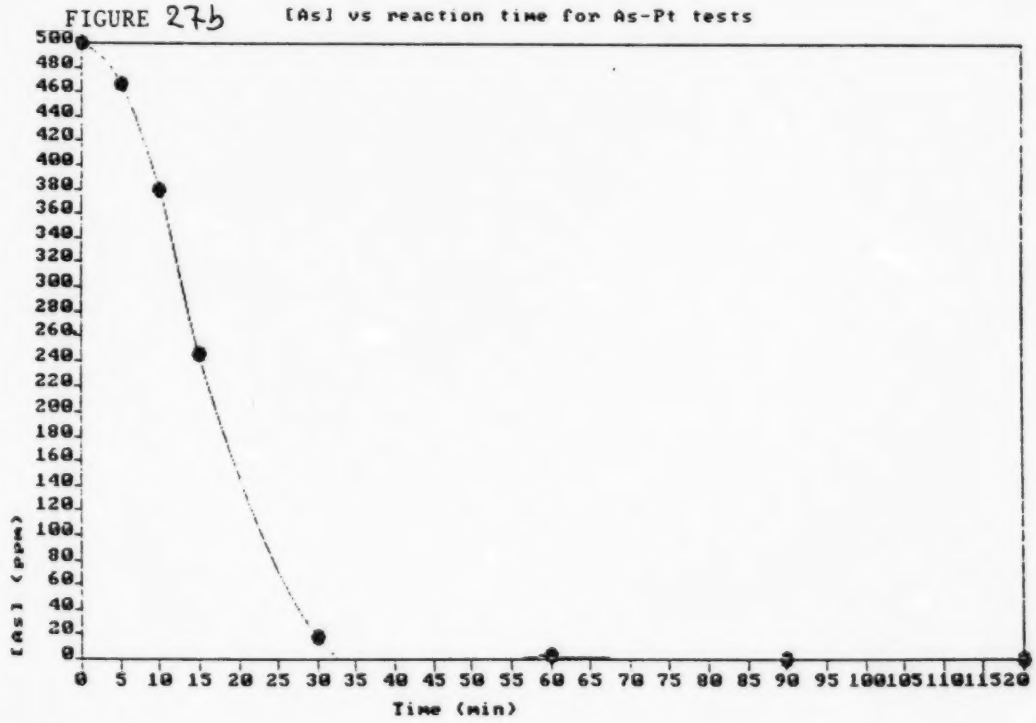


Fig. 27 Hydrogen reduction of a Pt(IV)/As(III) binary solution.

FIGURE 28a [Pd] vs reaction time for Cu-Pd tests

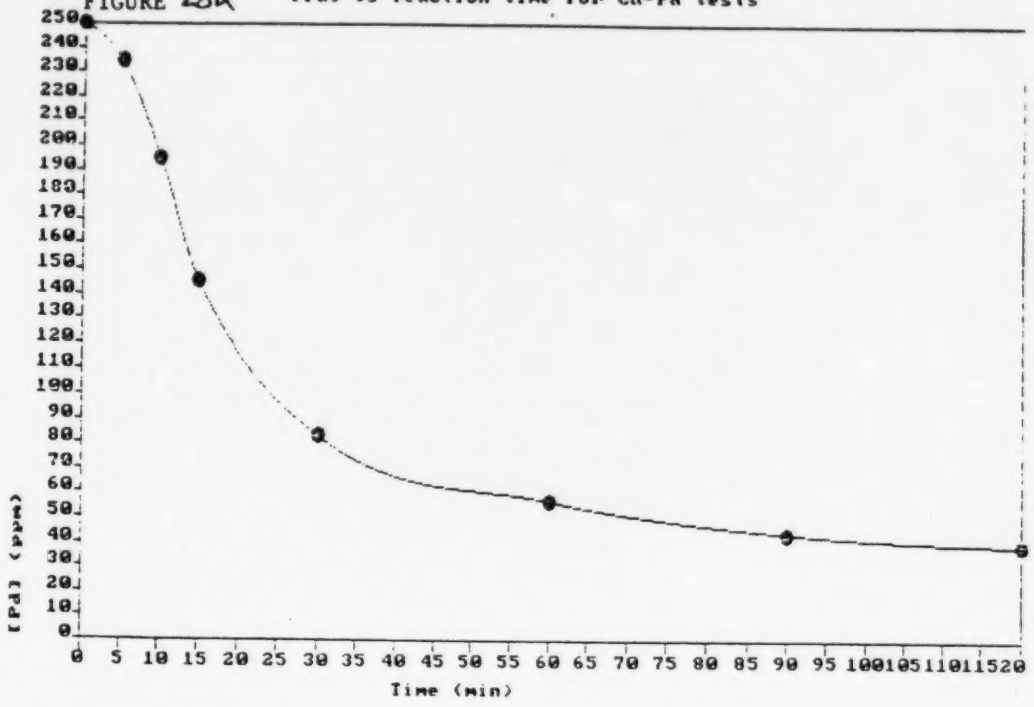


FIGURE 28b [Cu] vs reaction time for Cu-Pd tests

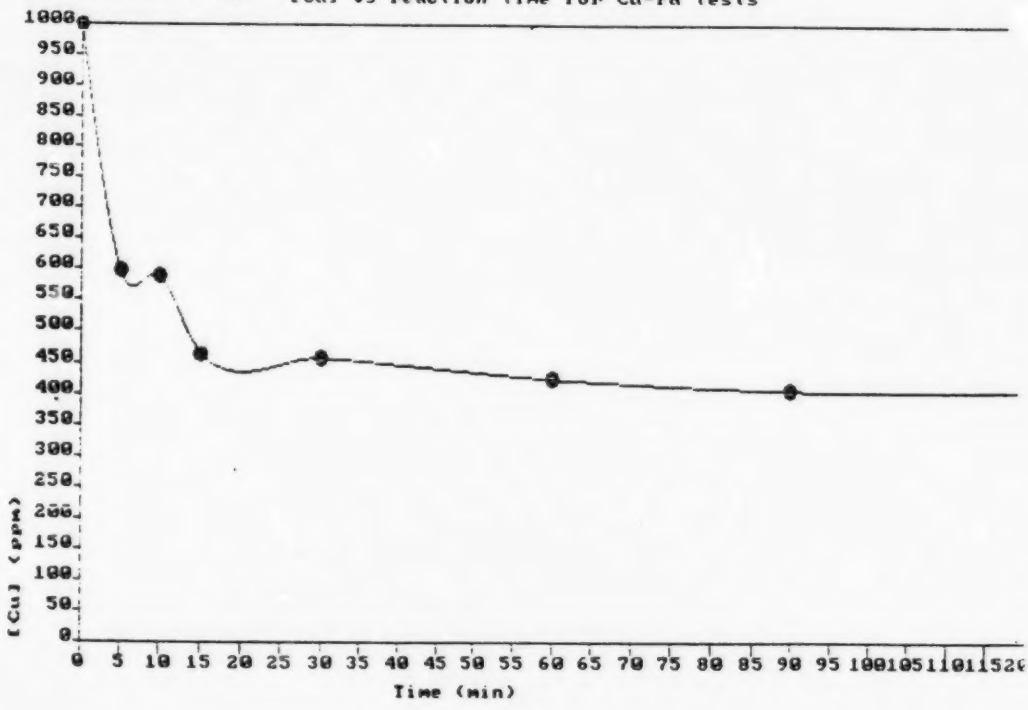


Fig. 28 Hydrogen reduction of a Pd(II)/Cu(II) binary solution.

FIGURE 29a [Pt] vs reaction time for Cu-Pt tests

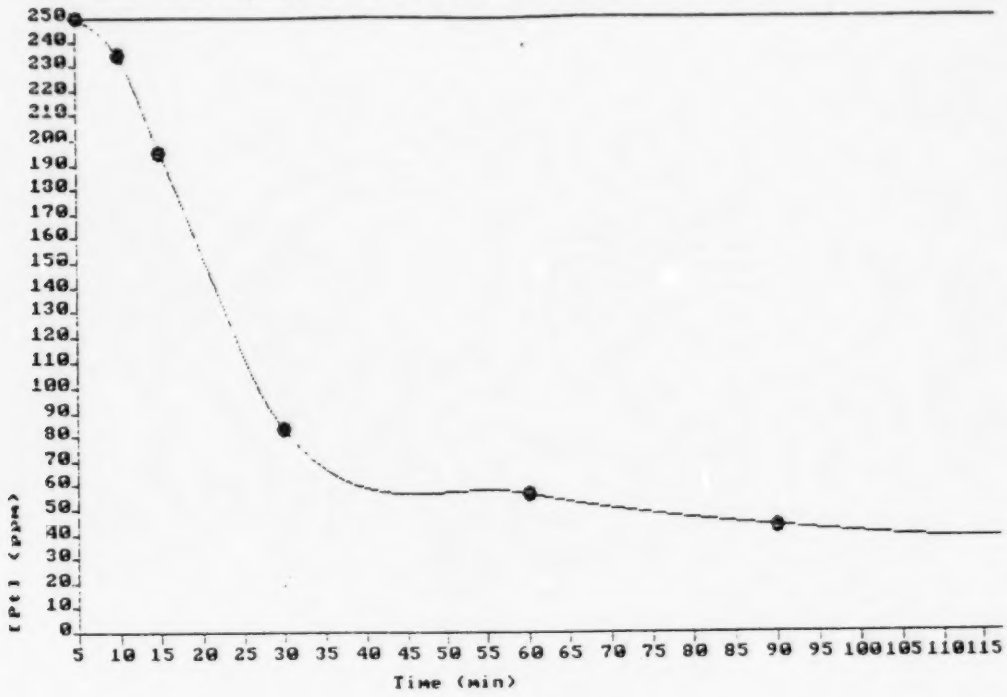


FIGURE 29b [Cu] vs reaction time for Cu-Pt tests

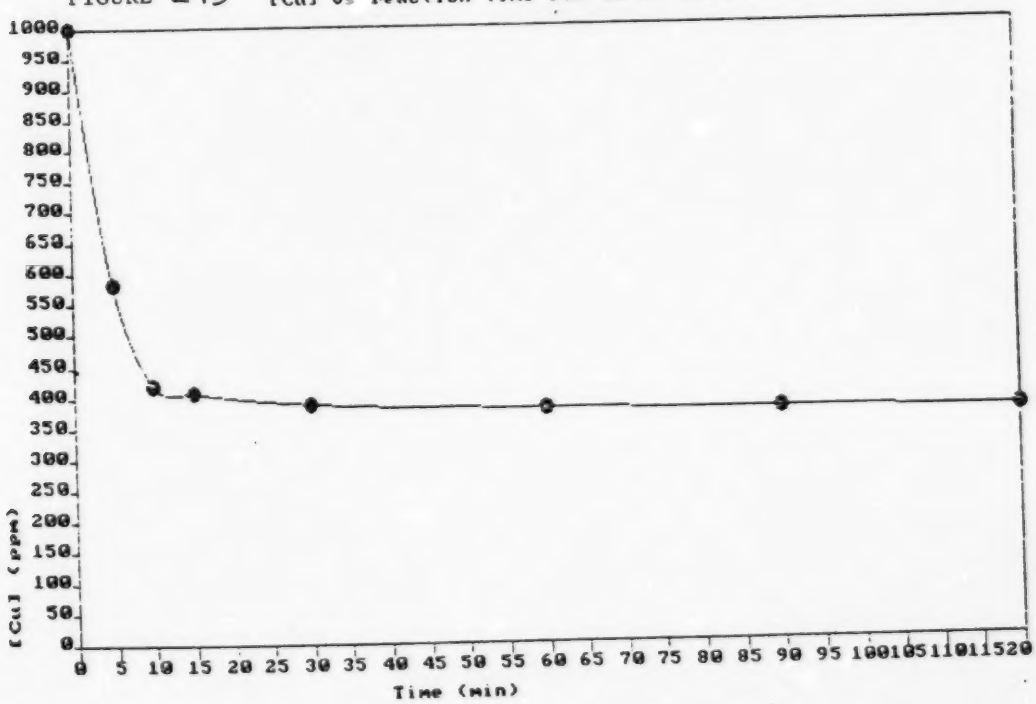


Fig. 29 Hydrogen reduction of a Pt(IV)/Cu(II) binary solution.

FIGURE 30α [Pd] vs reaction time for Pb-Pd tests

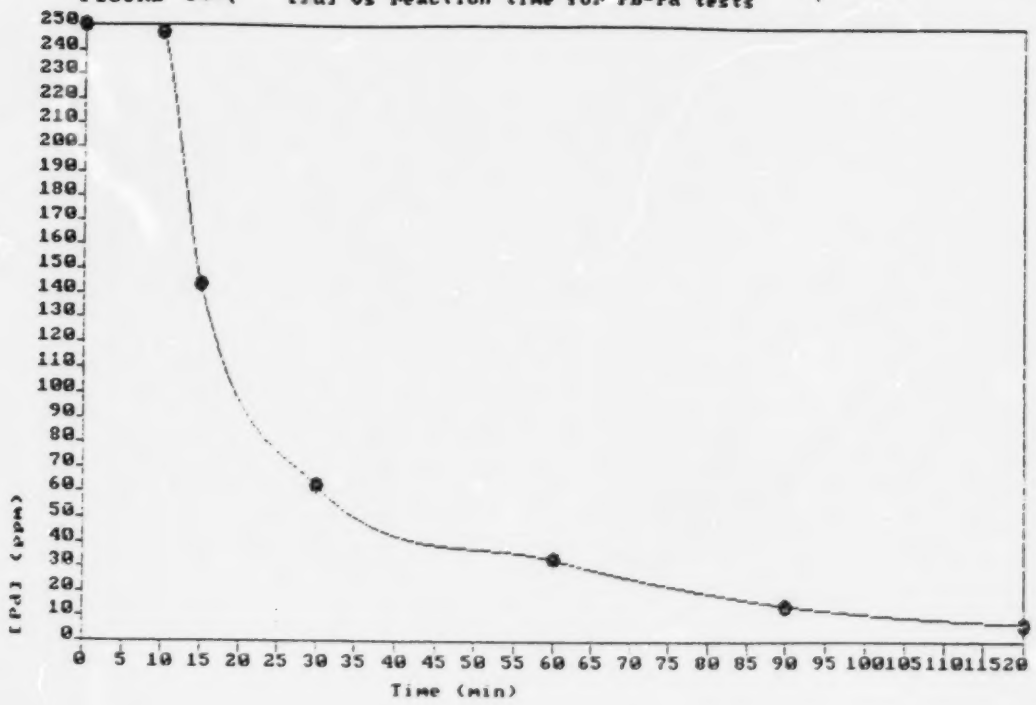


FIGURE 30b [Pb] vs reaction time for Pb-Pd tests

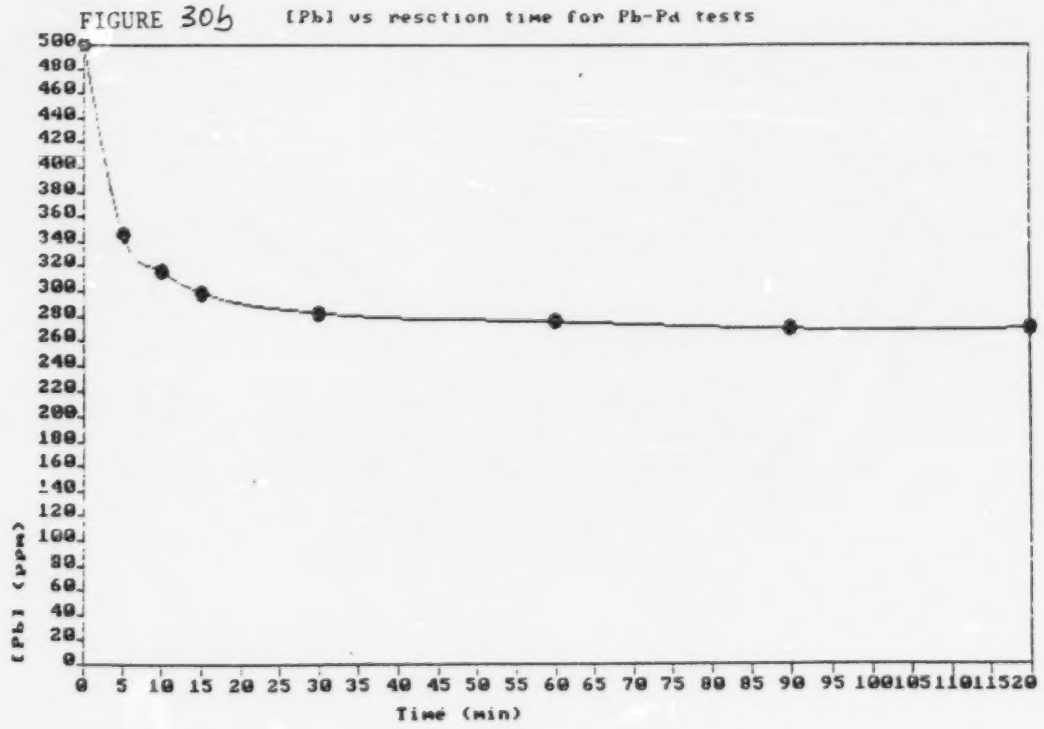


Fig. 30 Hydrogen reduction of a Pd(II)/Pb(II) binary solution.

FIGURE 31a [Pt] vs reaction time for Pb-Pt tests

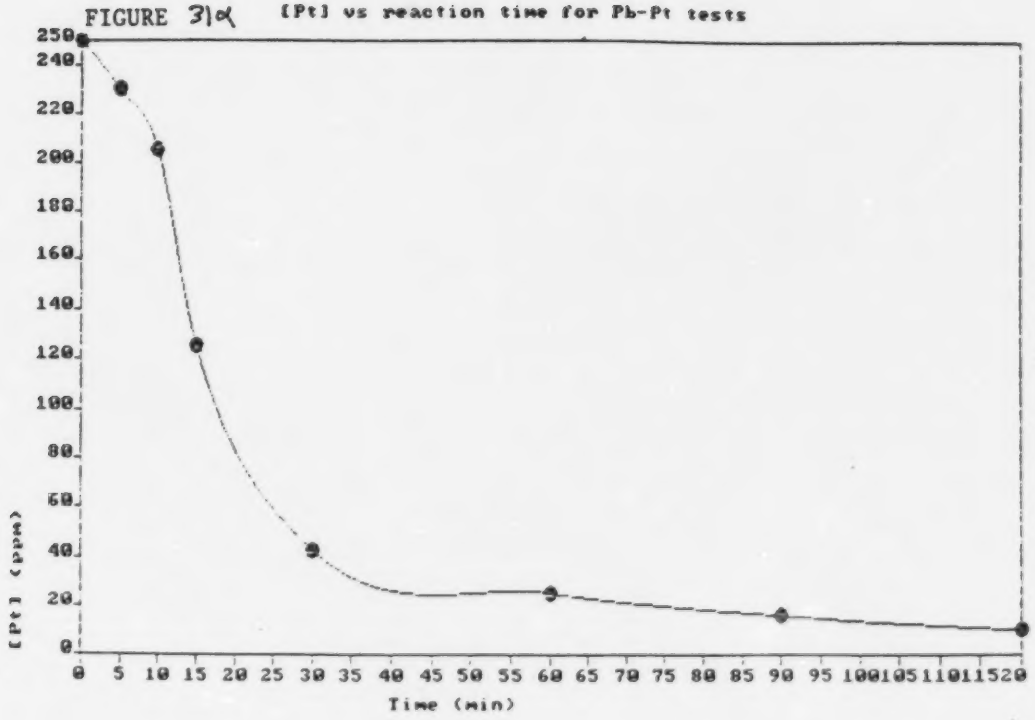


FIGURE 31b [Pb] vs reaction time for Pb-Pt tests

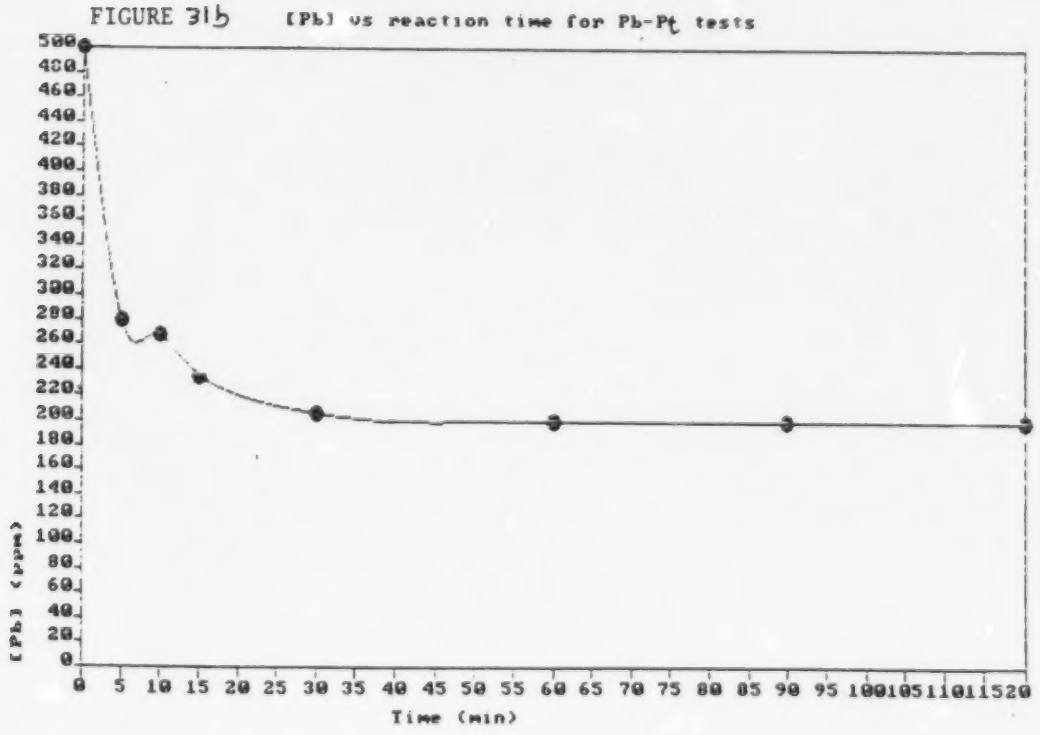


Fig. 31 Hydrogen reduction of a Pt(IV)/Pb(II) binary solution.

Pt/Pd Separation

No selectivity in Pt/Pd precipitation was exhibited (Fig. 32). Both metals precipitated out of solution in 10 minutes.

Multi-Metal Solution

Finally a hydrogen reduction test was performed using a composite solution having the following composition 4.5 g/l Pt(IV), 2.3 g/l Pd(II), 6.67 g/l Cu(II), 2 g/l Fe(III), 2 g/l Zn(II), 3 g/l Ni(II), 1.2 g/l Pb(II), 1.3 g/l Bi(III), 0.5 M HCl and 2 M NaCl. The reduction conditions were 75^{o}C, 50 psi H_2 and 2 hours reaction time. At the end of the experiment a massive precipitate was collected which was mostly adhered on the walls of the autoclave. No powder was formed. A typical micrograph of the precipitate is shown in Fig. 33. Microprobe analysis of the precipitate gave the following analysis 82% Pt, 8.4% Cu, 5% Pd, 4% Fe, 0.6% Ni. Periodic sampling during the experiment and AA analysis showed Pt precipitation to be almost complete (> 90%) while Pd precipitation represented only about 15% of the total metal. Pd(II) concentration after the first 30 min. remained basically constant at a level of ∿2.0 g/l. In other words it seems that Pd(II) acted within the tested reaction time as a hydrogenation catalyst facilitating the reduction of the metal cations present in the solution. It was rather surprising to detect

FIGURE 32a [Pd] vs reaction time for Pt-Pd tests

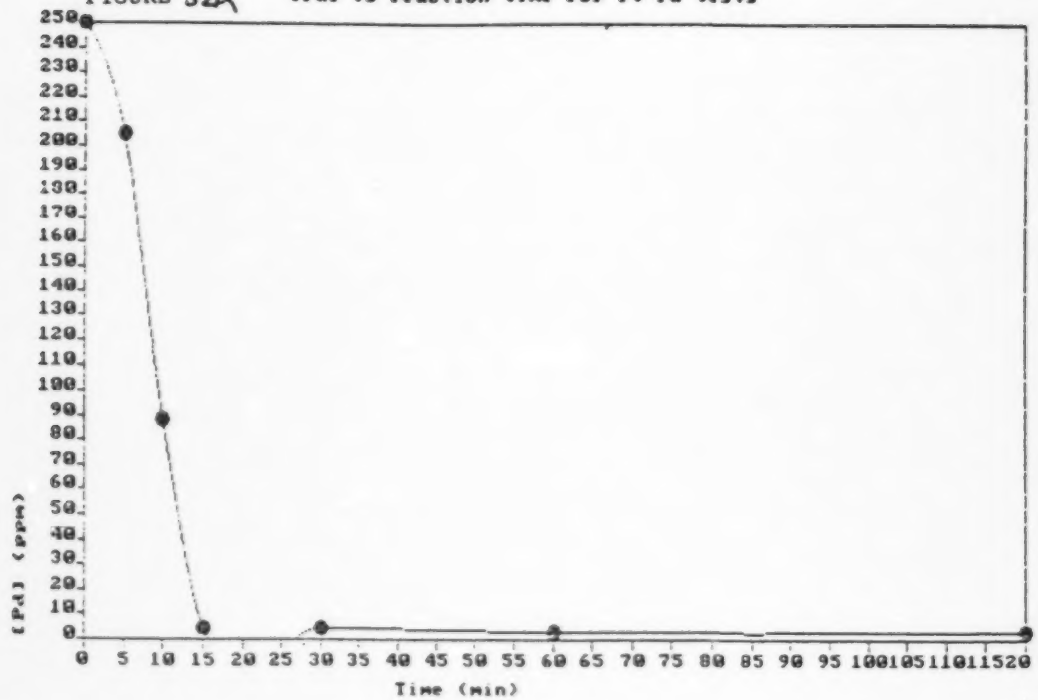


FIGURE 32b [Pt] vs reaction time for Pt-Pd tests

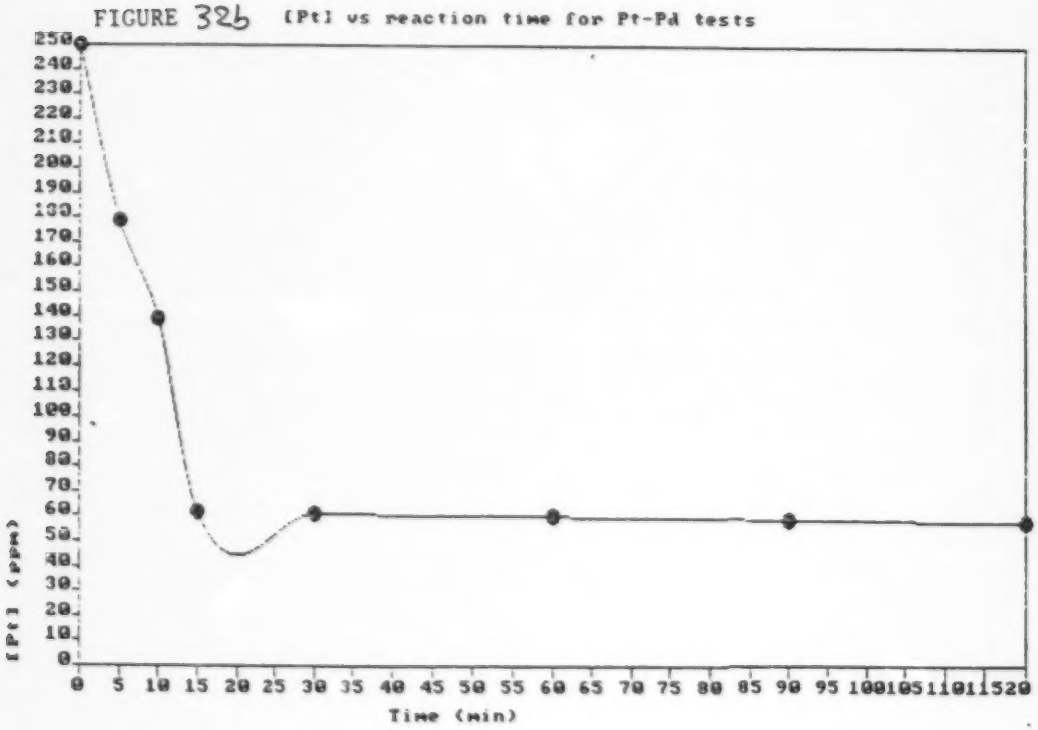


Fig. 32 Hydrogen reduction of a Pd(II)/Pt(IV) binary solution.

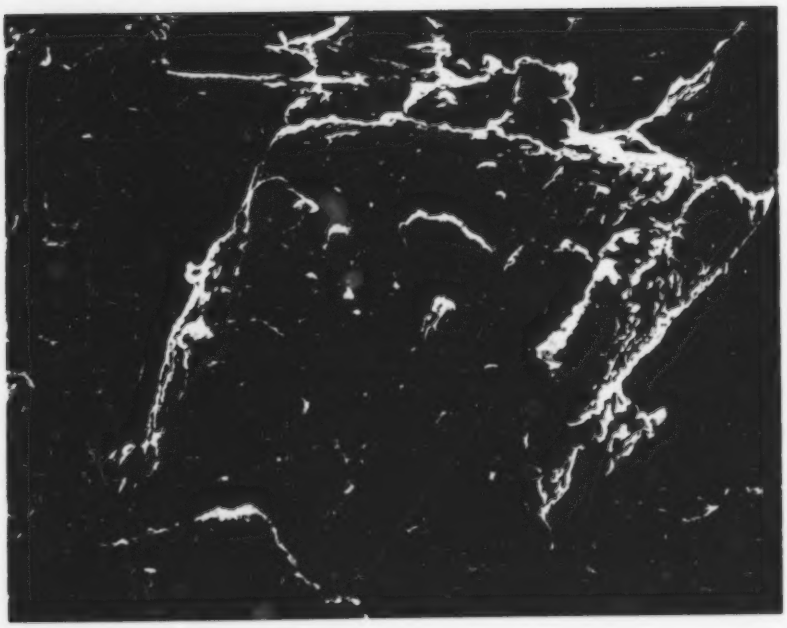


Fig. 33 Massive bulk Pt (82%) - Pd (5%) precipitate contaminated with base metals.

Fe and to a lesser degree Ni in the precipitate. Undoubtedly these results confirm the inability of hydrogen reduction to separate the precious metals from base metals.

Discussion

The presented results show that selective precipitation of Pd or Pt in the presence of base metals is not possible. Neither is the separation of the two metals. In addition to the contamination problem the presence of impurities appears to interfere also with the nucleation mechanism of the precious metals resulting thus in several instances in plating rather than powder production.

With the exception of Fe(III)/Fe(II) and Cu(II)/Cu(I) the reduction potentials of the base metal couples tested in this work possess values much lower than those of the precious metals (compare Table 3 with Table 1). Thus strictly speaking on thermocynamic grounds selectivity appears to be possible. However as the results of this work have showed this is not the case. This has to be attributed to the strong catalytic activity of Pd and Pt which activate the reduction of the base metals thus resulting in loss of selectivity. Thus hydrogenation appears to warrant application only to single metal solution following solvent extraction purification of the contaminated liquors. Finally the results of part B of the present investigation contradict the findings of earlier investigators (12) who had claimed separation of PGM with hydrogen.

Table 3. Standard reduction potentials of base metals chlor es (35) ($\alpha_{Cl^-} = 1$)

Metal Couple	E° (mV)
Fe(III)/Fe(II)	700
Cu(II)/Cu(I)	550
Cu(I)/Cu(O)	250
Sb(III)/Sb(O)	200
Bi(III)/Bi(O)	170
As(III)/As(O)	150
Pb(II)/Pb(O)	-150

PART C: DEPOSITION OF THIN METAL FILMS ON CERAMIC SUBSTRATES

In addition to fine metal powder production the method of hydrogen reduction from solution could also be used for thin metal coating of ceramic or other substrates. This approach has already been successfully utilized by Sherritt Gordon, Ltd. and a number of composite powders have been now commercially produced (36,37). The method involves suspension of the ceramic material in a solution carrying the metal to be deposited and pressurizing with H_2 at elevated temperatures. The method requires activation of the inert ceramic surface with the addition of surface-active reagents such as anthraquinone in order to enhance the heterogeneous catalytic activity of the substrate and thus produce uniform metal coating. This approach is particularly effective if the metal to be deposited on the ceramic material surface is nucleated only via a heterogeneous mechanism, as it is for example the case of Ni and Co. However this method is not equally effective for metals exhibiting both homogeneous and heterogeneous nucleation characteristics. In such cases other chemical reducing methods have to be used which could render the composite material contaminated with the oxidized products of the reduding agent - hydrogen being totally free of such complications. The above technique using hydrogen reduction in autoclave is not again well suited for the coating of rather large objects that cannot be kept in suspension.

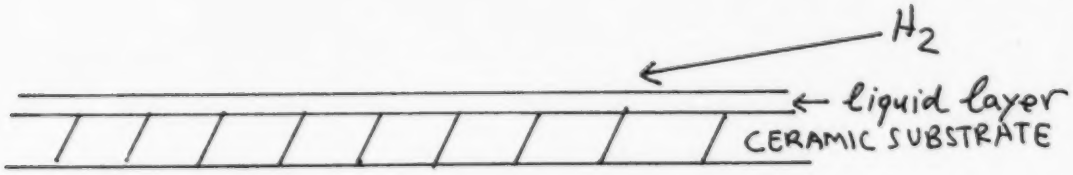
In the present work some preliminary tests were performed to assess the potential of using hydrogen reduction of Pd or Pt chloride solutions as a means to prepare thin metal films on zirconia material used in fuel cells. Sintered discs of the ZrO_2 material was provided by Dr. G. Pouskouleli. Only Pd reduction was attempted.

First, attempts to coat the ZrO_2 disc by suspension in solution and deposition of Pd via hydrogen reduction of the bulk $PdCl_2$ solution gave very poor results. Most of the metal precipitated as a powder away from the surface of the ceramic substrate. Apparently the strong homogeneous catalytic activity of $PdCl_4^{2-}$ was responsible for this behaviour. Addition of small amounts of anthraquinone in the solution in analogy to the method practiced by Sherritt Gordon, Ltd. (37) again failed to produce a satisfactory metal coating on the ZrO_2 surface.
It became evident thus that for the production of precious metal coatings on ceramic substrates a radically different approach from what so far has been practiced in conventional electroless plating industry had to be developed.

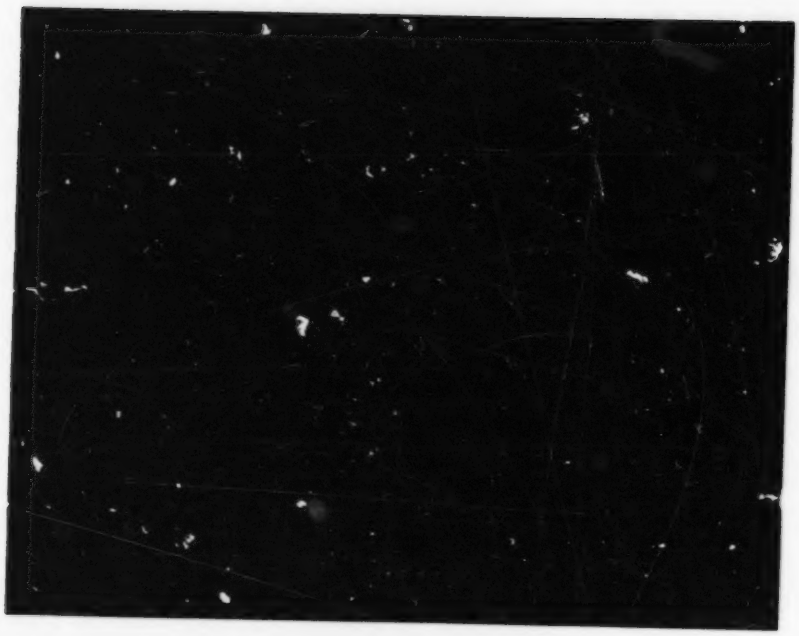
Liquid Layer Hydrogen Reduction Technique

The developed technique which is suitable for coating planar surfaces of ceramic substrates with Pt group metals involves the following:

The ceramic substrate is immersed in a Pd or Pt chloride solution and then is taken out of the solution and put on a flat surface. Then a stream of hydrogen gas is blown over the liquid layer (see the sketch below) and instantaneous precipitation



of the metal takes place. The formation of Platinum films with a similar procedure has been reported previously in the U.S.S.R.(38). By choosing the right concentration of PM (Pt or Pd) in the solution used to form the liquid layer or repeating the reduction procedure several times by replenishing the depleted liquid layer with fresh one, the thickness of the metal film can be adjusted accordingly. The procedure is carried out at room temperature and a low pressure



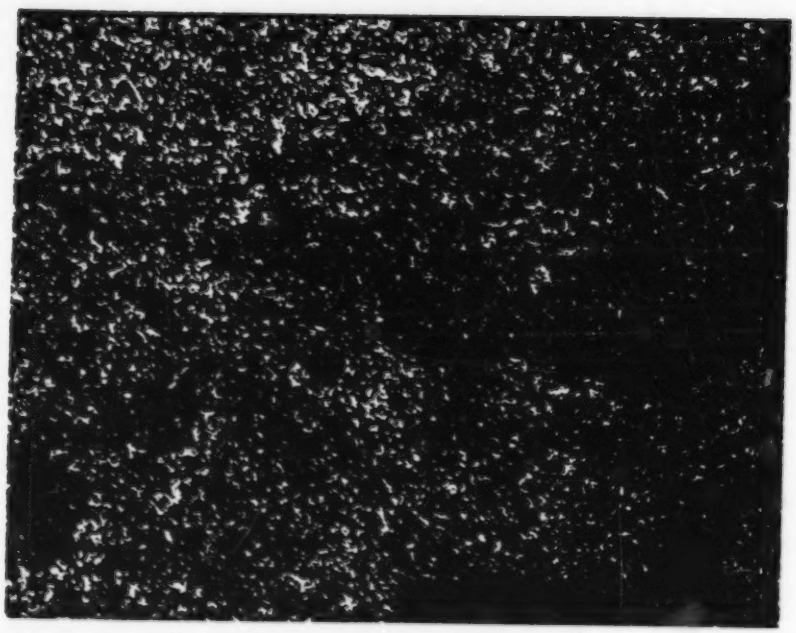


Fig. 34 Zirconia before (a) and after (b) Pd coating by the liquid layer hydrogen reduction technique.

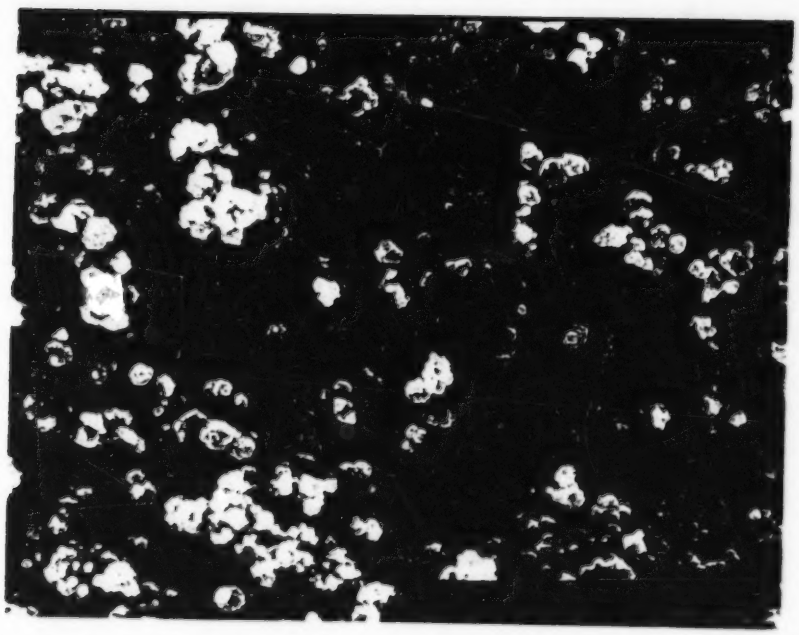


Fig. 35 Zirconia before (a) and after (b) Pd coating by the liquid layer hydrogen reduction technique.

hydrogen stream is used. The produced metal coating seems to be porous as it is required from the standpoint of fuel cell operation. In Figs. 34 and 35 microphotographs of the ceramic substrate (ZrO_2) taken before and after Pd coating using the method described above are shown. It can be clearly seen that the microstructure of the metal deposit consists of ultrafine Pd crystallites clustered together in aggregates. The metal deposit is not smooth and dense but rather porous (Fig. 35b) and cracked (Fig. 34b) which permit us to assume that high gas diffusion rates can be sustained in a possible fuel cell application. The thickness of the metal coating judging from the microphotographs of Figs. 34 and 35 appears to be in the order of few microns.

These preliminary results give rise to the interesting possibility of preparing thin films of Pt or Pd on ZrO_2 or other advanced ceramic materials with a rather simple and effective technique. Further work to optimize the procedure and characterize with various surface analytical techniques the thin metal coatings and the nature of the metal-ceramic bonding is needed.

5. CONCLUSIONS AND RECOMMENDATIONS

The recovery of gold, platinum and palladium powders by hydrogen reduction of their aqueous chloride solutions has been

studied in relation to a solvent extraction process recently developed by CANMET for the separation of precious metals. A number of conclusions and recommendations are made as a result of this work and they are summarized below.

1. Quantitative recovery of Pd and Pt from the two solvent extraction strip liquors is readily accomplished by hydrogen reduction under relatively mild temperature and pressure conditions. No expensive autoclaves but rather conventional glass reaction vessels can be used for this process. Recovery of gold powders by hydrogen precipitation was found on the other hand not to be possible.

2. Adjusting the solution composition to promote homogeneous rather than heterogeneous nucleation is critical in obtaining fine metal powders that could find applications in electronics. The solutions arising from the solvent extraction process circuit are ideally suited for production of fine metal powders since they contain traces of the organic solvent which by adsorption on the metal particles control their morphology and size.

3. The role of organic additives in controlling the size and morphology of the produced particles and preventing the aggregation of the fine particles via secondary coagulation

requires further study. Prevention of aggregation during precipitation of fine particles from solution is very important not only for precious metal powders but also for the preparation of fine ceramic and composite powders.

4. Separation of Pt/Pd by hydrogen reduction is not feasible. Neither is the selective precipitation of Pt or Pd from a solution containing base metals. The results of the present study render thus previously published information which had claimed separation of PGM/BM with H_2 as unreliable. Also no powder but rather a massive precipitate which adheres on the walls of the precipitation vessel is produced when base metal impurities are present in the solution.

5. Hydrogen reduction of Pt/Pd chloride solutions can be used to coat ceramic substrates with thin metal films provided that the reaction is carried out in a liquid layer rather than in the bulk of the solution. This technique which was developed in the present investigation shows promise and further work is warranted.

6. Finally the production of composite powders by heterogeneous deposition of metal films on ceramic substrates via hydrogen reduction of aqueous or organic solutions is worthy of further consideration. This method offers the potential of

producing uniform and dense metal coatings as opposed to electroplating which due to current density fluctuations results in non-homogeneous metal deposits. This method of composite powder production which was first conceived and practiced by Sherritt-Gordon, Ltd. could be extended to be used with organic rather than aqueous solutions. An organic medium offers the following advantages: (i) the homogeneous activity of the metals can be controlled by strong complexation, (ii) it permits the precipitation of metals such as Fe and Cd that cannot be produced otherwise in an aqueous medium, (iii) it produces totally homogeneous metal surfaces and (iv) it is not corrosive.

Acknowledgements

The technical assistance of Dr. S. Kelebek, Mr. V. Petropoulos, Mr. V. Aprahamian and Mr. G. Karkas with the experimental programme is gratefully acknowledged.

References

1. B.D. Rowan, "The Role of Precious Metal Powders in Electronics", Precious Metals 1982, Ed. M.I. El Guindy, Pergamon Press, (1983), pp 259-268.

2. K.C. Yang and B.D. Rowan, "Production of Gold, Platinum, and Palladium Powders", Metals Handbook, Ninth Edition, Vol. 7, AMS, Metals Park, OH, (1984), pp 148-151.

3. G.P. Demopoulos, "Solvent Extraction in Precious Metals Refining", J. of Metals, Vol. 38(6), (1986), pp 13-17.

4. G.P. Demopoulos, G. Pouskouleli and P.J.A. Prud'homme, "Direct Recovery of Precious Metals by Solvent Extraction and Selective Removal", U.S. Pat. No. 4,654,145, 1987.

5. G.P. Demopoulos, G. Pouskouleli and G.M. Ritcey, "A Novel Solvent Extraction System for the Refining of Precious Metals", ISEC'86, Proc. Int. Solv. Extr. Conf. (1986), Vol. 2, pp 581-588.

6. G. Pouskouleli, S. Kelebek and G.P. Demopoulos, "Recovery and Separation of Platinum and Palladium by Coextraction and Differential Stripping", Separation Processes in Hydrometallurgy, Ed. G.A. Davies, Ellis Horwood Publishers, England, (1987), pp 174-188.

7. G.P. Demopoulos, "Direct Recovery of Gold-Precious Metals from Loaded Organics with Hydrogen", Final Report DSS Contract Serial No. OST84-00327 (June 1985) 35 pages.

8. G.P. Demopoulos, "Direct Recovery of Gold-Precious Metals from Loaded Organics with Hydrogen", Final Report DSS Contract Serial No. OST85-00056 (July 1986) 51 pages.

9. G.P. Demopoulos and G. Pouskouleli, "Hydrochemical Preparation of Fine Precious Metal Powders", Journal of Metals, Vol. 40, June 1988, in press.

10. F. Habashi, "Principles of Extractive Metallurgy: Vol. 2 Hydrometallurgy", Gordon and Breach, New York (1970), pp. 252-257.

11. V.V. Ipatieff, Jr. and V.G. Tronev, "The Mechanism of the Removal of Noble Metals from Solutions of their Salts by Hydrogen under Pressure", Chemical Abstracts, Vol. 29 (1935), 4658.

12. V.V. Ipatieff, Jr. and V.G. Tronev, "The Separation of the Platinum Metals by Hydrogen under Pressure", Chemical Abstracts, Vol. 29, (1935), 5770.

13. V.G. Tronev and S.M. Boudin, "Reduction of Gold from Chloride and Cyanide Solutions with Hydrogen under Pressure", Chemical Abstracts, Vol. 45 (1951), 55.

14. M. Findlay, "The Use of Hydrogen to Recover Precious Metals", Precious Metals 1982, Ed. M.I. El Guindy, Pergamon Press (1983), pp 477-501.

15. MITSUI MINING AND SMELTING, "Recovery Platinum Metals from Spent Platinum Series Catalyst by Dissolving Catalyst in Hydrochloric Acid in Chlorine Presence and Reducing with Gas", Japan Pat. No. 58-45125 (1983).

16. A.J. Bard, R. Parsons and J. Jordan, Eds. "Standard Potentials in Aqueous Solution", Marcel Dekker, Inc., New York, (1985), p. 318, 343, 353, 354, 385, 388.

17. J. Halpern, J.F. Harrod and P.E. Potter, "Catalytic Activation of Hydrogen in Aqueous Solution by the Chloropalladate (II) Ion", Can. J. Chem. Vol. 37, (1959), pp 1446-1450.

18. J.F. Harrod and J. Halpern, "Catalytic Activation of Molecular Hydrogen in Solution by Chlororhodate (III) Complexes", Can. J. Chem. Vol. 37 (1959), pp 1933-1935.

19. J.F. Harrod, S. Ciccone and J. Halpern, "Catalytic Activation of Molecular Hydrogen by Ruthenium(III) Chloride Complexes", Can. J. Chem., Vol. 39(1961), pp 1372-1376.

20. J. Halpern, "Homogeneous Catalytic Activation of Molecular Hydrogen by Metal Ions", Advances in Catalysis, Vol. 9(1957), pp 302-311.

21. J. Halpern, "The Catalytic Activation of Hydrogen in Homogeneous, Heterogeneous and Biological Systems", Adv. in Catalysis, Vol. 11(1959), pp 301-370.

22. G.C. Bond, "Homogeneous and Heterogeneous Catalysis by Noble Metals", Homogeneous Catalysis: Industrial Applications and Implications, Ed. B.J. Luberoff, Advances in Chemistry Series, Vol. 70, ACS, Washington, D.C. (1968), pp 25-34.

23. F. Linke and A. Seidell, "Solubilities", Vol. II, Am. Chem. Soc. Washington, D.C. (1958).

24. A.E. Pitts, J.C. Van Loon and F.E. Beamish, "The Determination of Platinum by Atomic Absorption Spectroscopy, Part I, Air-acetylene flames", Anal. Chim. Acta., Vol. 50, (1970), pp 181-194.

25. O.A. Short, "Gold Powder for Printed Circuit Inks", U.K. Patent No. 1,313,826, 1973.

26. A. Bilodeau, G.B. Harris, K. Hooper, C.A. MacDonald and R.W. Stanley, "Silver Refinery Anode Slimes Treatment at the CCR Division of Noranda Inc.", paper presented in the TMS-AIME Symposium "The Electrorefining and Winning of Copper", Denver CO, February 1987.

27. N.P. Finkelstein and R.D. Hancock, "A New Approach to the Chemistry of Gold", Gold Bulletin, Vol. 7(3)(1974), pp 72-77.

28. M. Boudart, "Kinetics of Chemical Processes", Prentice Hall, Inc. (1968), pp 136-137.

29. O. Ginstrup and I. Leden, "The Equilibrium between Platinum (0), Platinum(II), and Platinum(IV) in a Chloride Ion Medium at 60°C", Acta Chem. Scand. Vol. 21(1967), pp 2689-2694.

30. D.M. Considine and G.D. Considine, Eds., "Encyclopedia of Chemistry", Van Nostrand Reinhold Co., New York, (1984), p. 78, 162.

31. D.H. Napper, "Colloid Stability", Ind. Eng. Chem. Prod. Res. Develop. Vol. 9(4)(1970), pp 467-477.

32. T.F. Tadros, "Suspensions" in "Surfactants" Ed. T.F. Tadros, Academic Press, (1984), pp 197-220.

33. D.H. Napper, "Steric Stabilization", J. Coll. Interf. Sci., Vol. 58(2) (1977), pp 390-407.

34. R. Hogg and K.C. Yang, "Secondary Coagulation", J. Coll. Interf. Sci. Vol. 56(3), 1976, pp 573-576.

35. D.M. Muir and G. Senanayake, "Principles and Applications of Strong Salt Solutions to Mineral Chemistry", Extraction Metallurgy '85, M.J. Jones (Ed.) IMM London, (1985), pp 65-91.

36. B. Meddings, "Production of Composite Powders", Metals Handbook, Ninth Edition, Vol. 7, AMS, Metals Park OH, (1984) pp 173-175.

37. W. Kunda, "New Developments in the Preparation of Composite Powders", High Temperatures-High Pressures Vol. 3 (1971) pp 593-612.

38. N.V. Demenev, A.S. Shur, and G.G. Fedorova, "The Structure of Metallic Films Obtained on the Surface of Aqueous Solutions of Metal Salts by Action of Reducing Gases I. The Structure of Platinum Films, Kolloid Zhur. Vol. 11 (1949), pp 289-98; Chemical Abstracts Vol. 44 (1950), No. 901.